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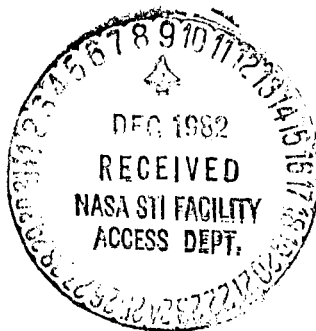
SIXTH SEMI-ANNUAL PROGRESS REPORT

NASA-CR-170129  
19830012871

# Evaluation of High Temperature Structural Adhesives for Extended Service

CONTRACT NAS1-15605

SUBMITTED TO  
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
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NF02584

FIFTH SEMI-ANNUAL PROGRESS REPORT

EVALUATION OF HIGH TEMPERATURE STRUCTURAL  
ADHESIVES FOR EXTENDED SERVICE

Contract NAS1-15605

Submitted to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
LANGLEY RESEARCH CENTER

May 1981

THE BOEING AEROSPACE COMPANY

P.O. Box 3999

Seattle, Washington 98124

183-21144#

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## FOREWORD

This report was prepared by the Boeing Aerospace Company, Kent, Washington, under Contract NAS1-15605, "Evaluation of High Temperature Structural Adhesives for Extended Service." It is the fifth semi-annual technical progress report detailing work performed between 2 November 1980 and 2 May 1981. The program is sponsored by the National Aeronautics and Space Administration, Langley Research Center (NASA-LRC). Mr. J. B. Nelson is the project monitor for NASA-LRC.

Performance of this contract is under the direction of the Materials Technology department of the Boeing Aerospace Company. Mr. J. C. Johnson is program manager and Mr. C. L. Hendricks is technical leader. Mr. S. G. Hill is principal investigator. Major contributors to this program are:

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## SUMMARY

The long term thermal aging data initiated in Phase I is reported. All candidate adhesive systems have exhibited significant degradation in bond properties after 505K (450°F) 10,000 hour exposure. Failures appear to be adhesive in the oxide layer. Phase II chemical characterization, cure cycle studies, baseline data, preliminary specifications, and environmental exposure data generated on polyphenylquinoxaline is presented. Similar but limited data on LARC-13 and NR056X adhesives is reported. Evaluation of LARC-TPI has been delayed due to late delivery of material.

## 1.0 INTRODUCTION

Contract NAS1-15605 is a NASA-LRC program to develop technology to support Supersonic Cruise Research (SCR). The primary objective of this contract is to evaluate and select adhesive systems for SCR applications and demonstrate elevated-temperature environmental durability for extended periods (approximately 50,000 hours). Boeing's development approach is to evaluate leading adhesive resins and surface preparation techniques for bonding titanium structure, optimize processes, and establish durable adhesive systems (adhesive, surface preparation, and primer) capable of extended service at 505K (450°F).

Program efforts are divided into two phases. Phase I, Adhesive Screening, is a 12-month study to evaluate ten adhesive resins and eight titanium surface treatments, resulting in the selection of two adhesive systems for more extensive evaluation. Phase II, Adhesive Optimization and Characterization, is an optional 24-month study dependent upon successful results from Phase I. It is divided into two tasks. Task 1 optimizes the two selected systems, provides necessary specifications, and generates a moderate data base. Figures 1-1 and 1-2 illustrate the program flow for Phases I and II, respectively. Figures 1-3 and 1-4 show Phase I and II significant events and schedules, respectively.

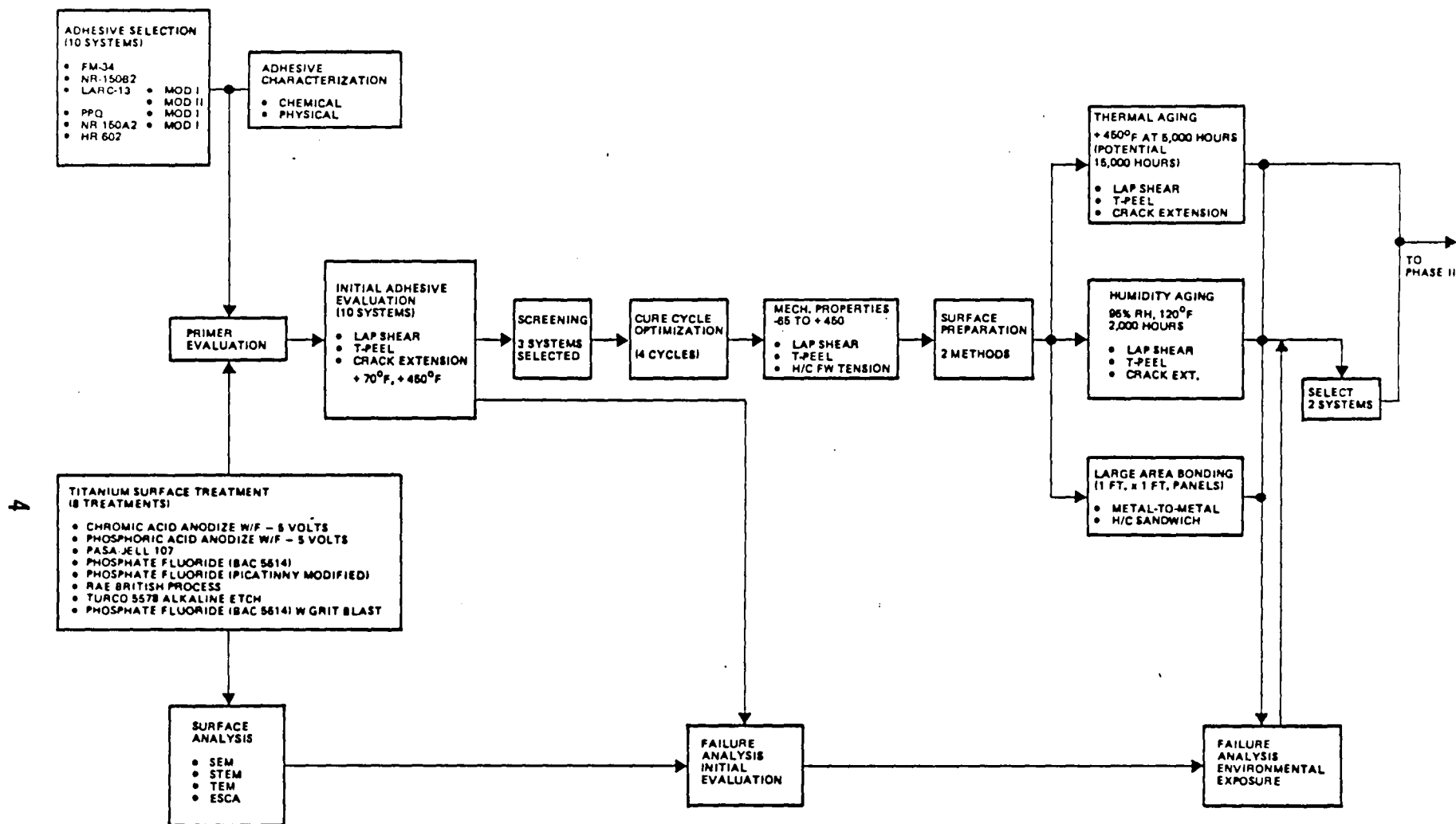


Figure 1-1: Phase I, Flow Diagram

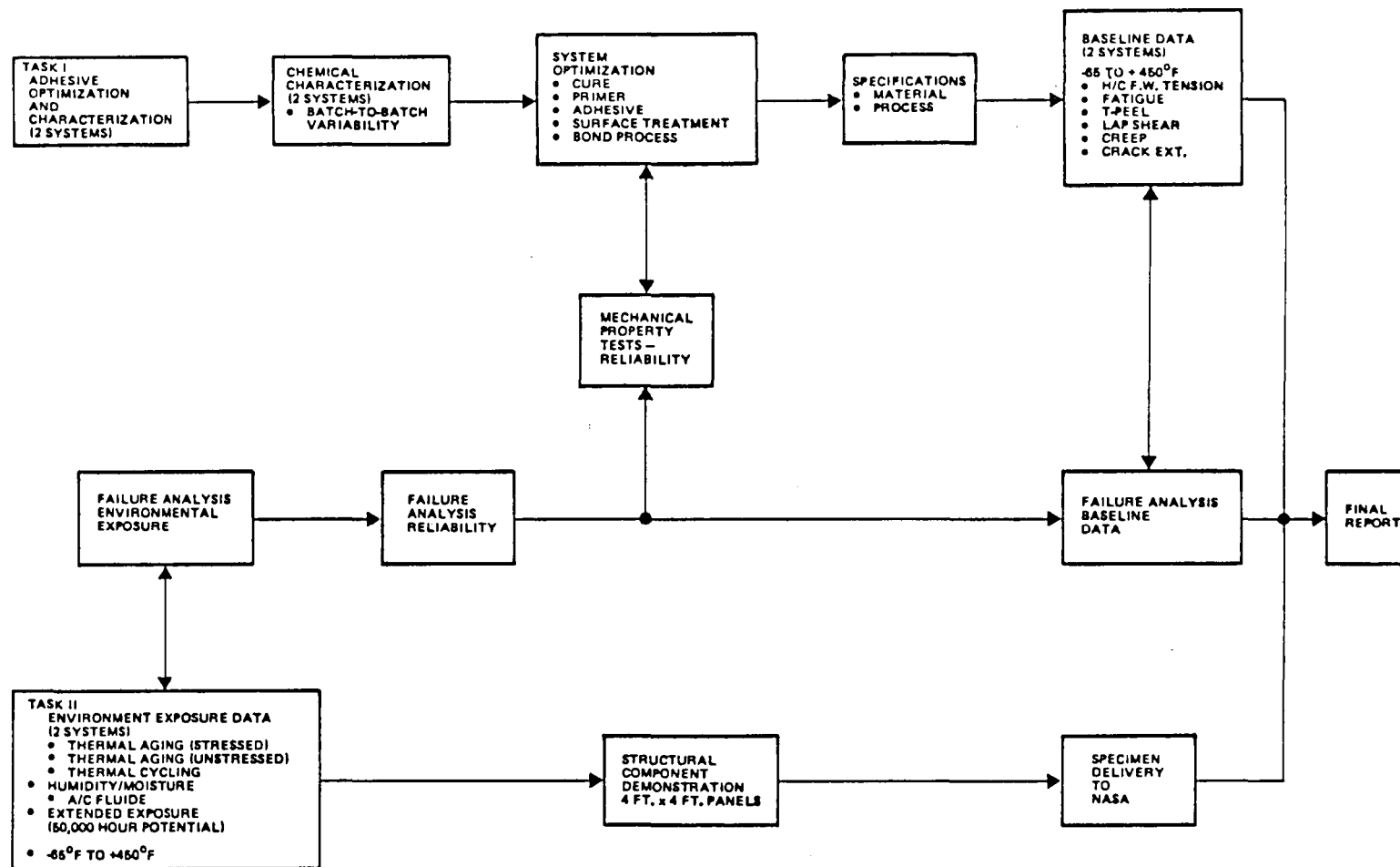


Figure 1-2: Phase II, Adhesive Optimization and Characterization Flow Diagram

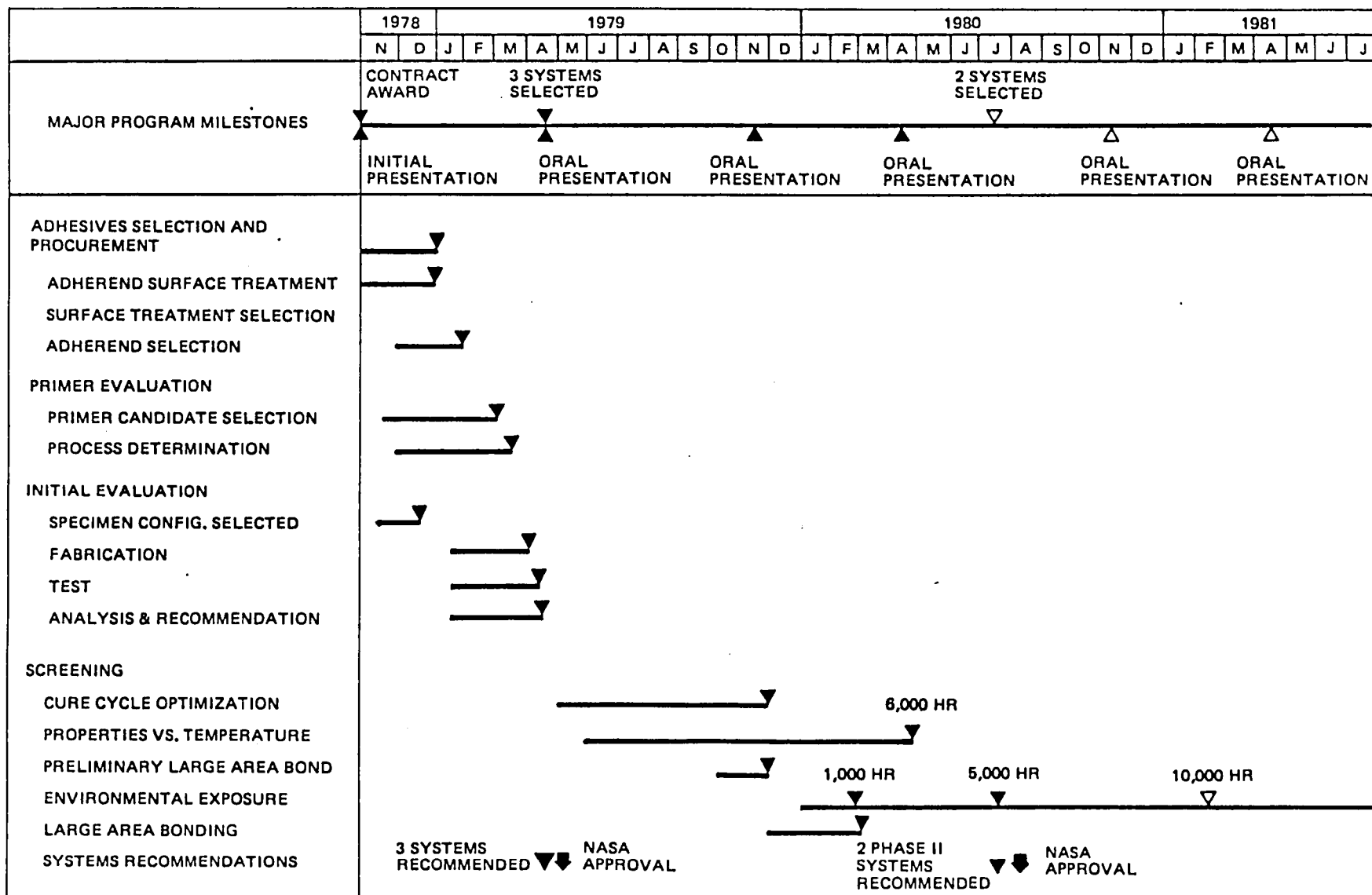


Figure 1-3: Phase I Adhesive Screening Program Schedule

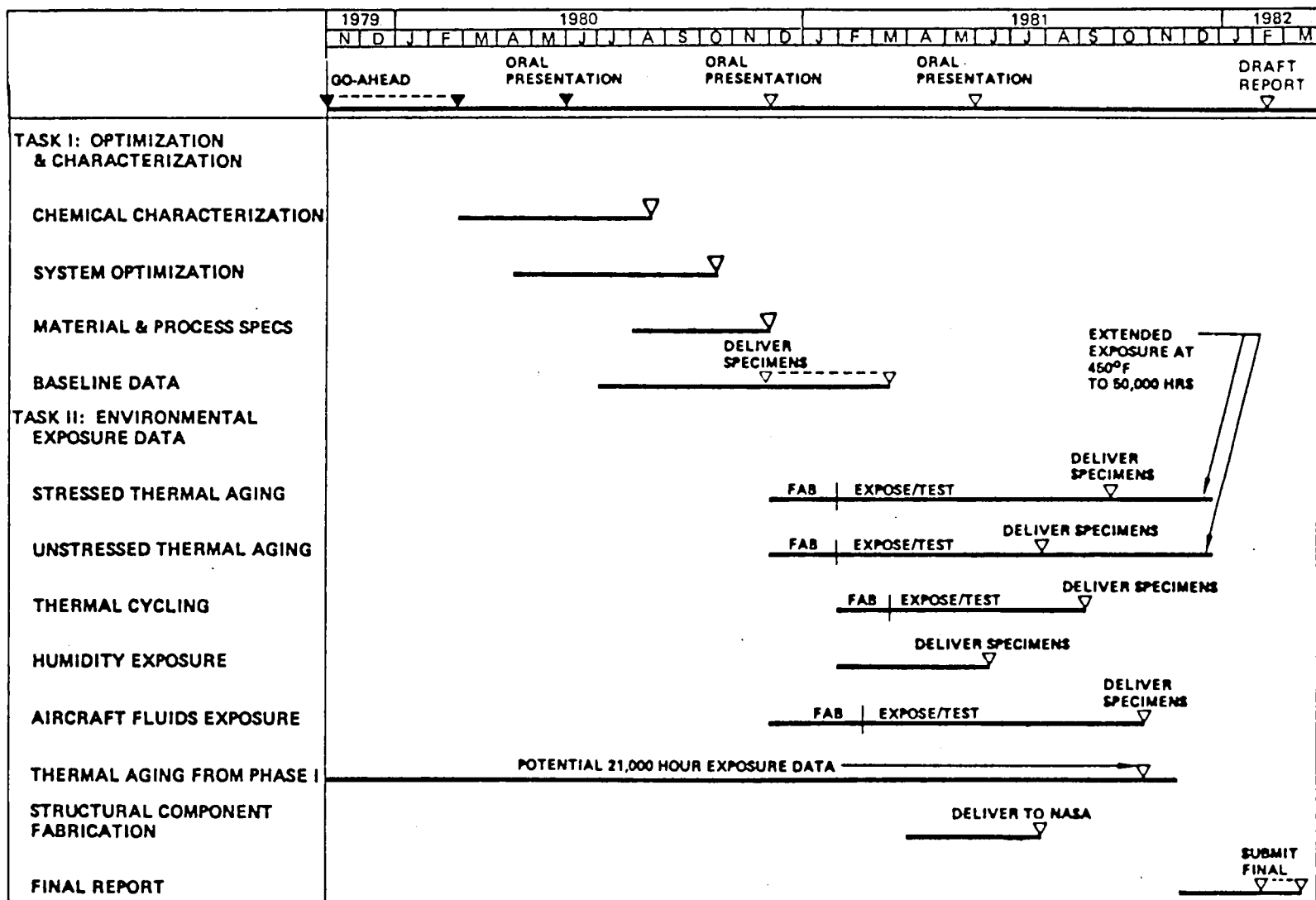


Figure 1-4: Program Schedule Phase II, Adhesive Optimization and Characterization

## 2.0 TECHNICAL DISCUSSION

### 2.1 PHASE I—SURFACE TREATMENT STUDY

This portion of the program is evaluating the effects of 322K (120°F)/95% relative humidity (RH) and 505K (450°F) thermal aging on two different titanium surface treatments for each of the three adhesives.

LARC-13 surface treatments are:

- o Pasa-Jell 107
- o Chromic acid anodize, 10 volts

NR056X surface treatments are:

- o Pasa-Jell 107
- o Chromic acid anodize, 10 volts

PPQ surface treatments are:

- o Chromic acid anodize, 5 volts
- o Chromic acid anodize, 10 volts

Figures 2.1-1 through -12 illustrate the data obtained to 10,000 hours. Tables 2.1-1 through -14 list the summary value averages and individual test coupon values.

The coupons remaining will fulfill the requirements for long-term 505K (450°F) and 322K (120°F)/95% RH exposure requirements for Phase I. Coupons exposed to 322K (120°F)/95% RH have been tested at 5000 hours. Coupons exposed to 505K (450°F) have been tested at 10,000 hours.

#### 2.1.1 Analysis of LARC-13 Data

The 322K (120°F)/95% RH data, shown in Figures 2.1-1 and 2.1-3 and as listed in Tables 2.1-3 and 2.1-5, indicates that LARC-13 is unaffected by moisture to 5,000 hours. Ten volt chromic acid anodize shows some strength advantage over Pasa Jell.

NAS1-15605 TITANIUM SURFACE TREATMENT STUDY  
EFFECT OF 322°K (120°F)/95% RH UPON ADHESIVE CRACK EXTENSION  
LARC-13

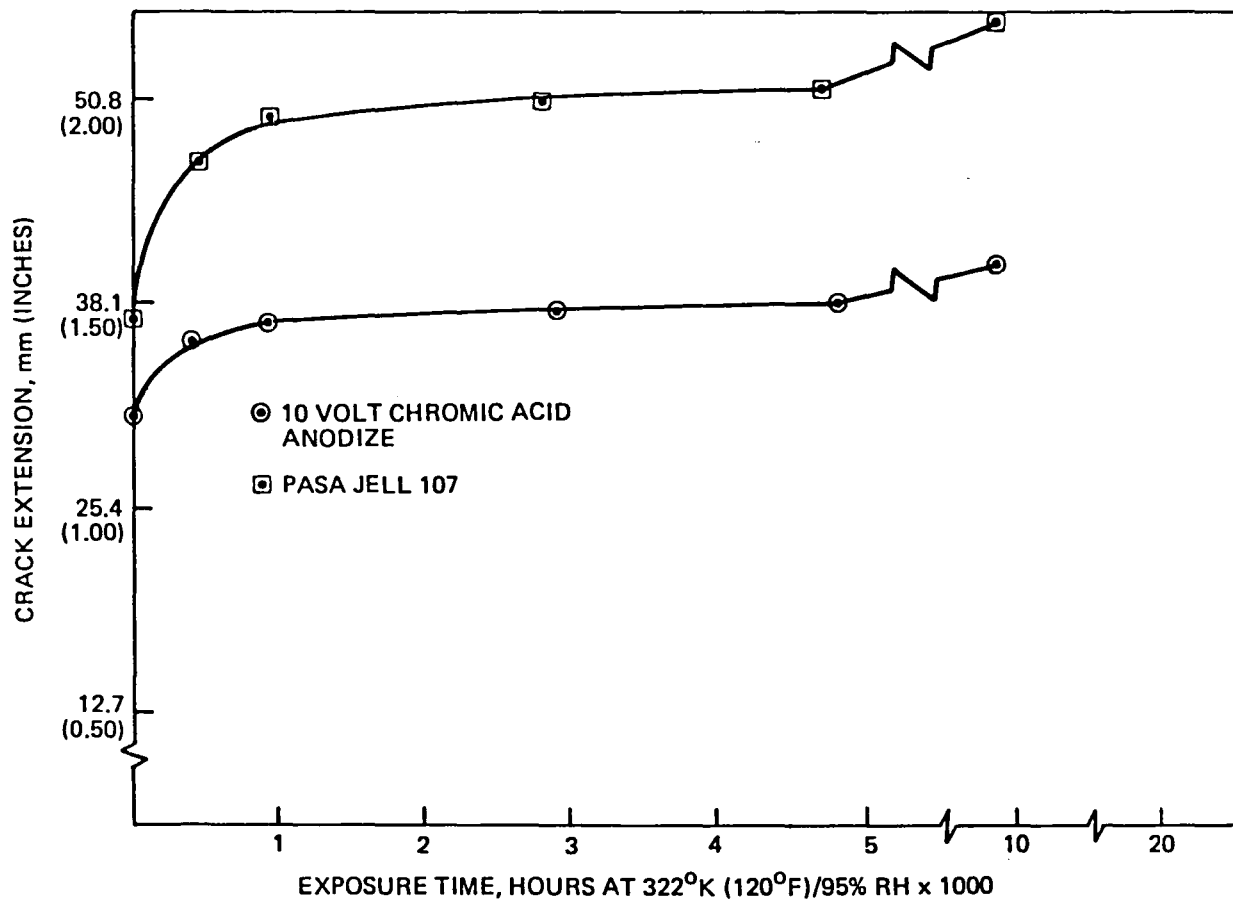


Figure 2.2-1:

NAS1-15605 SURFACE TREATMENT STUDY  
EFFECT OF 505°K (450°F) EXPOSURE UPON ADHESIVE CRACK EXTENSION  
LARC-13

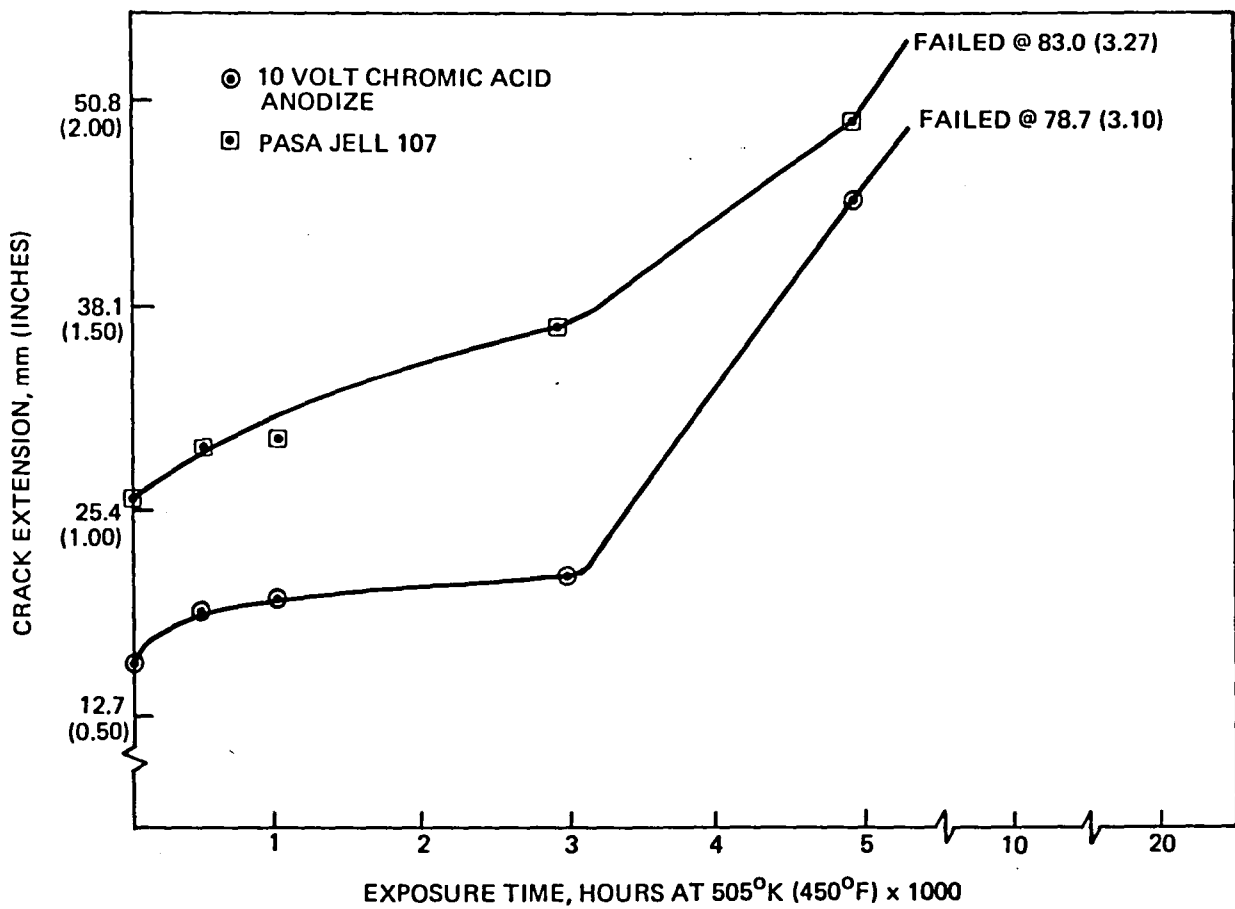


Figure 2.2-2:

NAS 1-15605 SURFACE TREATMENT STUDY  
EFFECT OF 322°K (120°F)/95% RH UPON ADHESIVE LAP SHEAR  
LARC-13

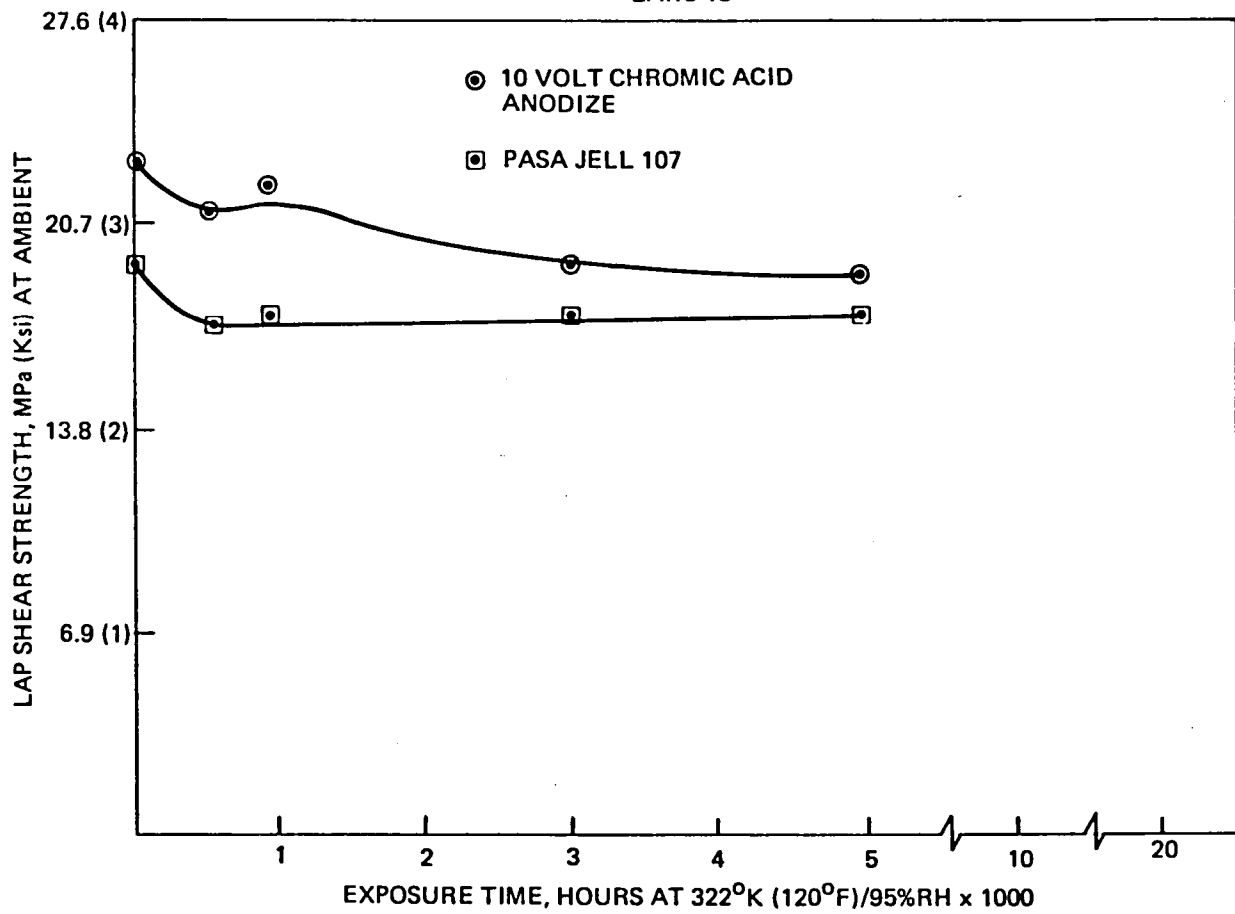


Figure 2.2-3:

NAS1-15605 SURFACE TREATMENT STUDY  
EFFECT OF 505°K (450°F) UPON ADHESIVE LAP SHEAR

LARC-13

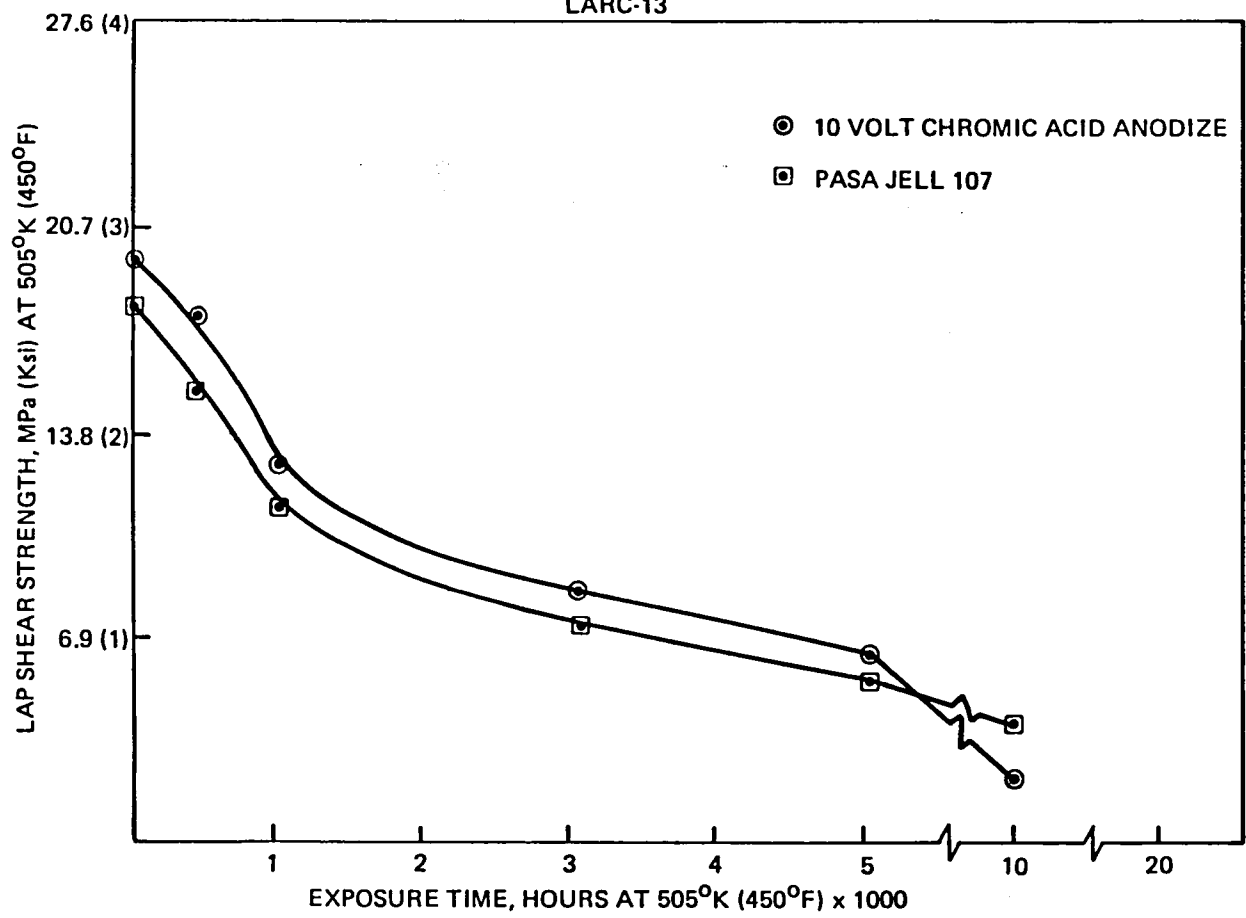


Figure 2.2-4

NAS1-15605 SURFACE TREATMENT STUDY  
EFFECT OF 322°K (120°F)/95% RH UPON ADHESIVE CRACK EXTENSION  
NR056X

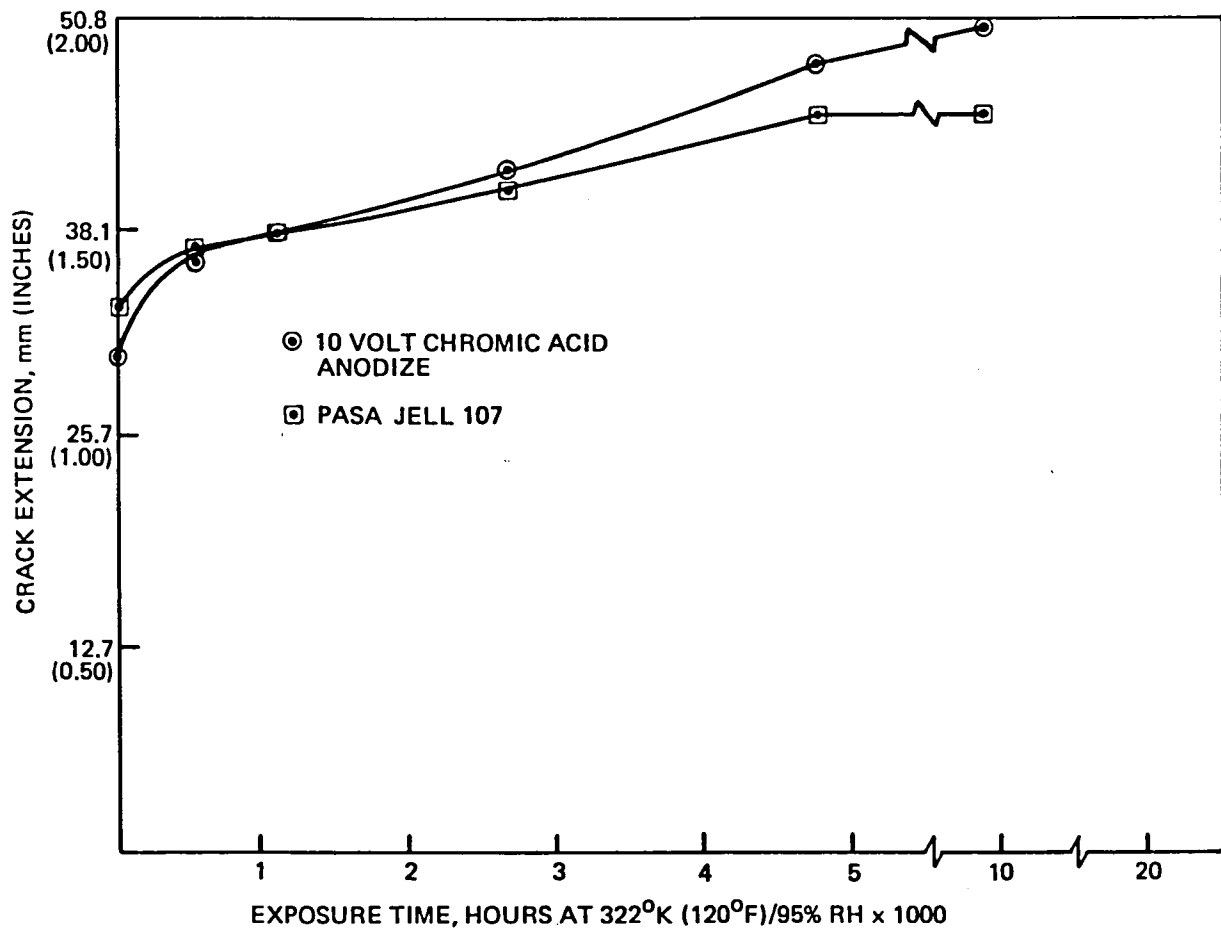


Figure 2.2-5

NAS1-15605 SURFACE TREATMENT STUDY  
EFFECT OF 505°K (450°F) EXPOSURE UPON ADHESIVE CRACK EXTENSION  
NR056X

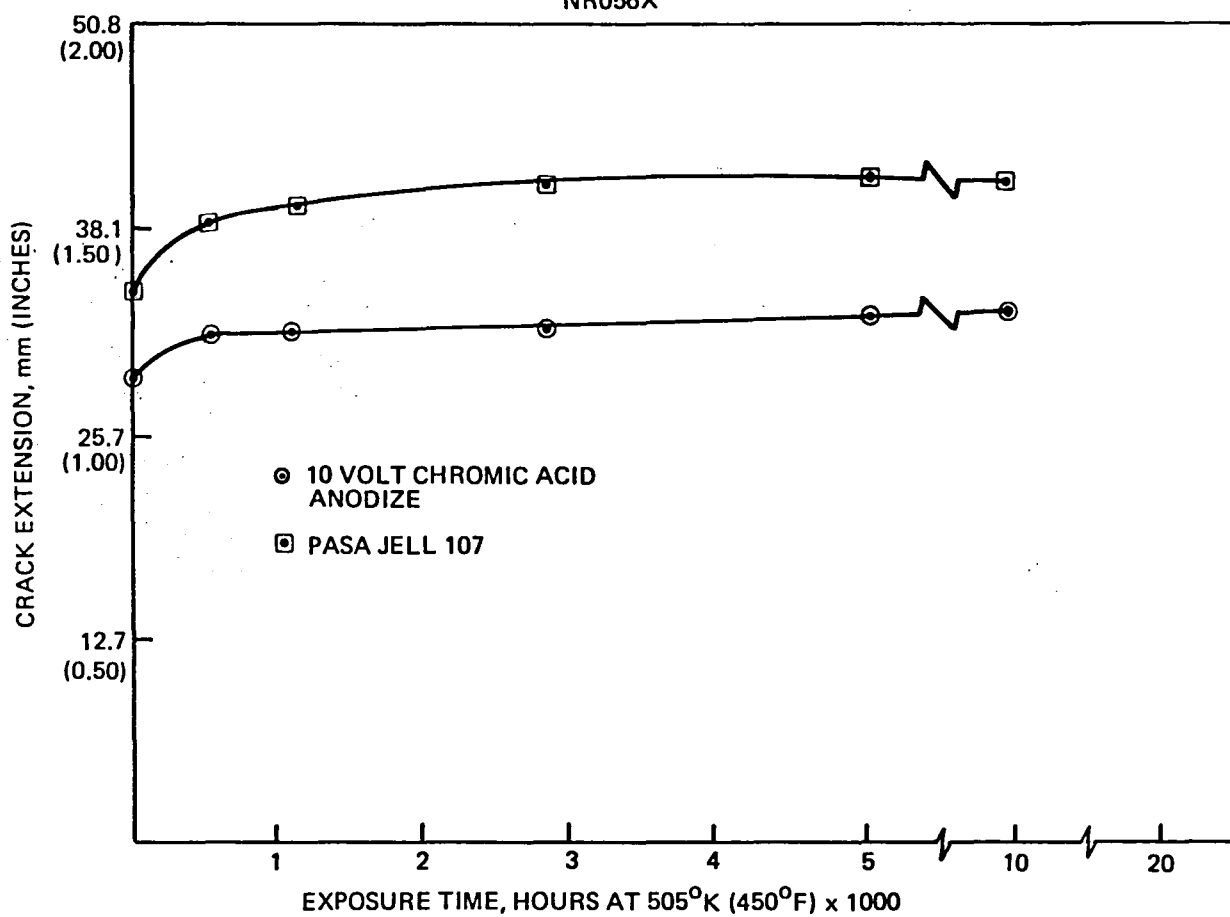


Figure 2.2-6:

NAS1-15605 SURFACE TREATMENT STUDY  
EFFECT OF 322°K (120°F)/95% RH UPON ADHESIVE LAP SHEAR  
NR056X

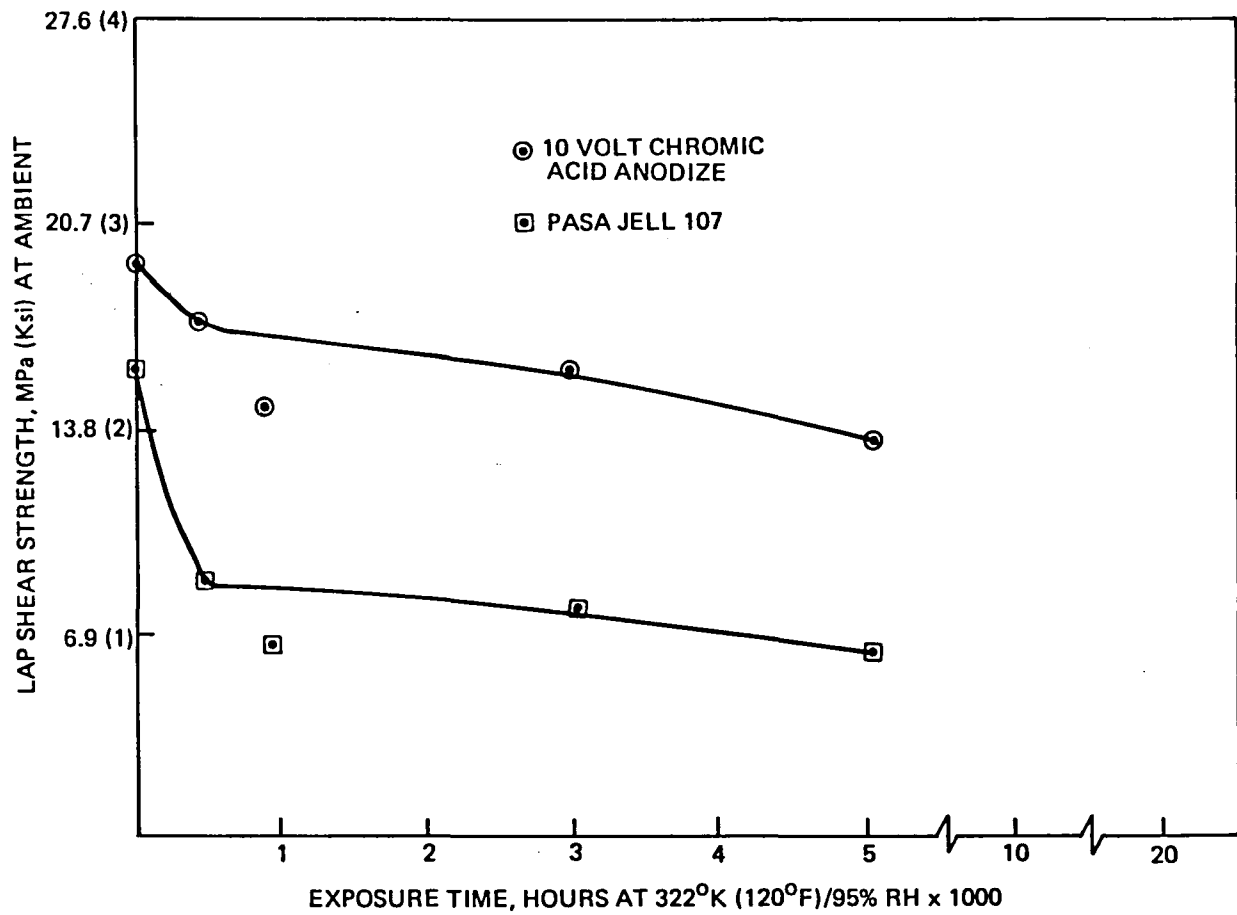


Figure 2.2-7:

NAS1-15605 SURFACE TREATMENT STUDY  
EFFECT OF 505°K (450°F) UPON ADHESIVE LAP SHEAR  
NR056X

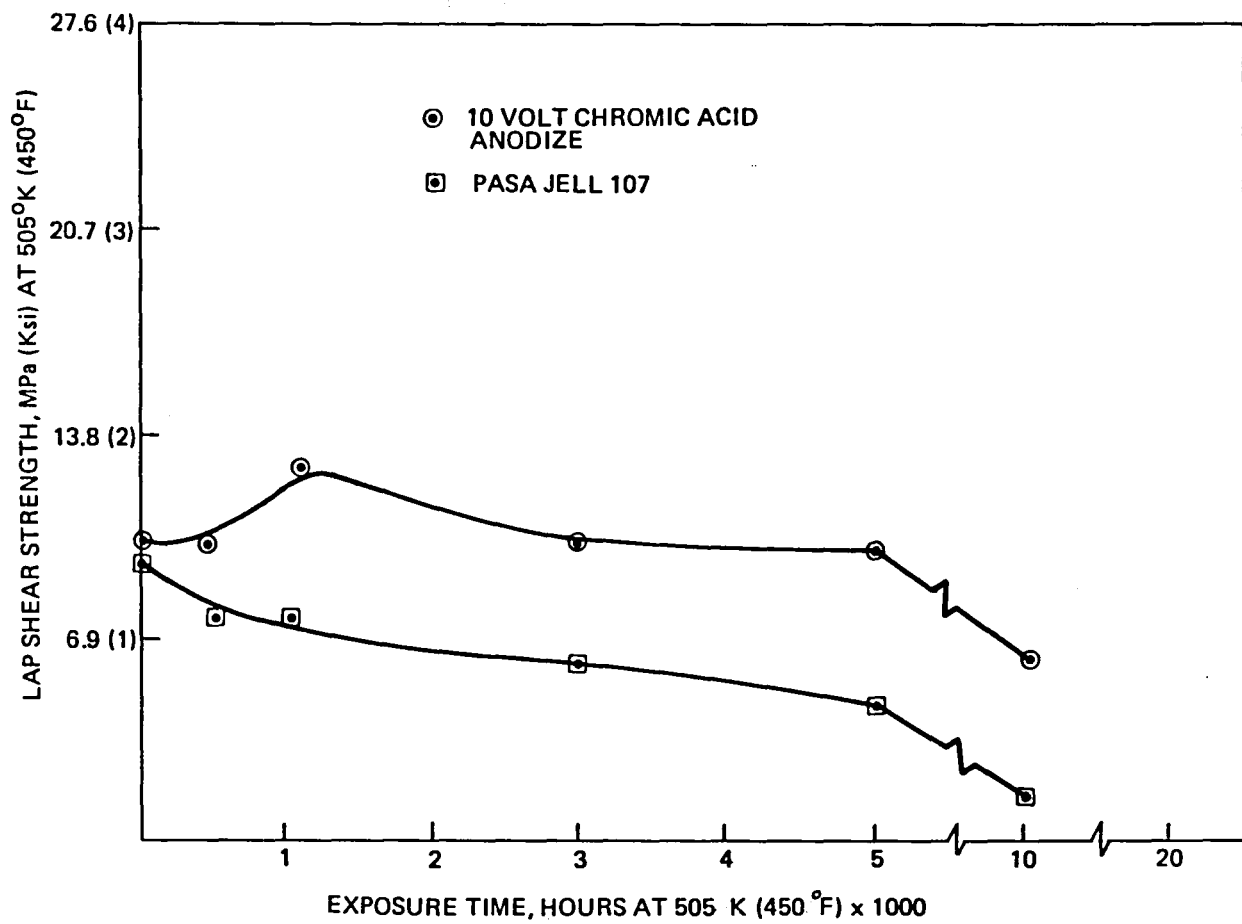


Figure 2.2-8:

NAS1-15605 SURFACE TREATMENT STUDY  
EFFECT OF 322°K (120°F)/95% RH UPON ADHESIVE CRACK EXTENSION  
POLYPHENYLQUINOXALINE

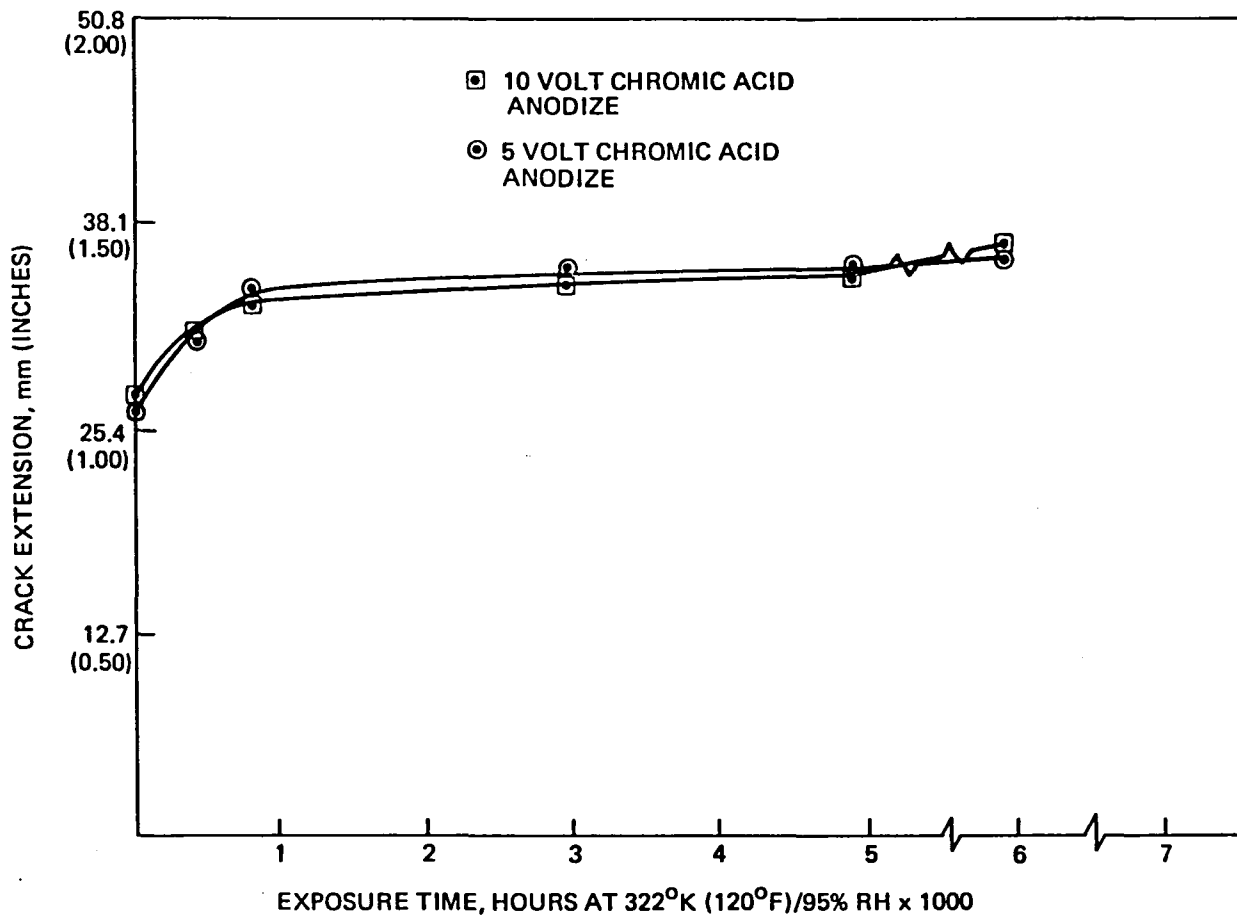


Figure 2.2-9:

NAS1-15605 SURFACE TREATMENT STUDY  
EFFECT OF 505°K (450°F) EXPOSURE UPON ADHESIVE CRACK EXTENSION  
POLYPHENYLQUINOXALINE

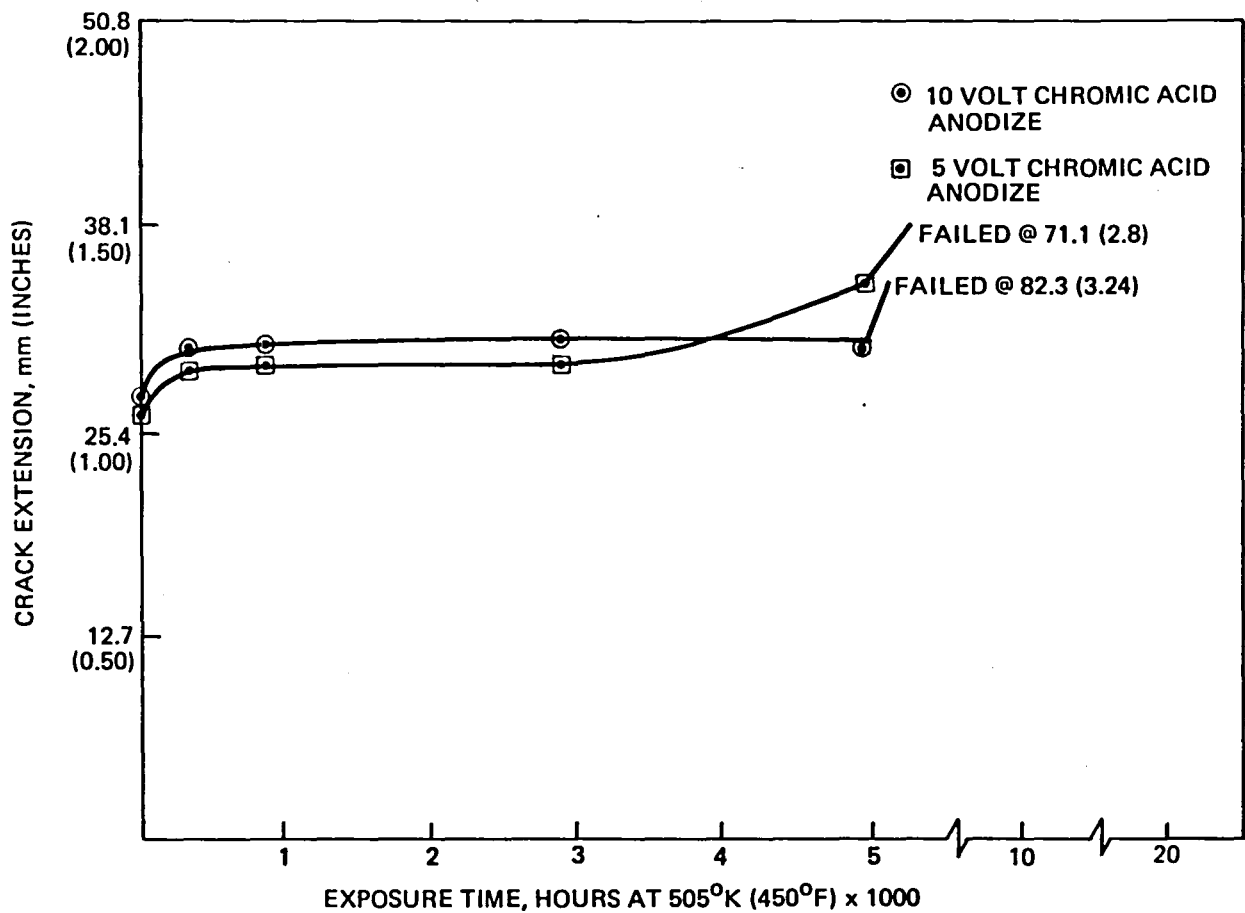


Figure 2.2-10:

NAS1-15605 SURFACE TREATMENT STUDY  
EFFECT OF 322K (120°F)/95% RH UPON ADHESIVE LAP SHEAR  
POLYPHENYLQUINOXALINE

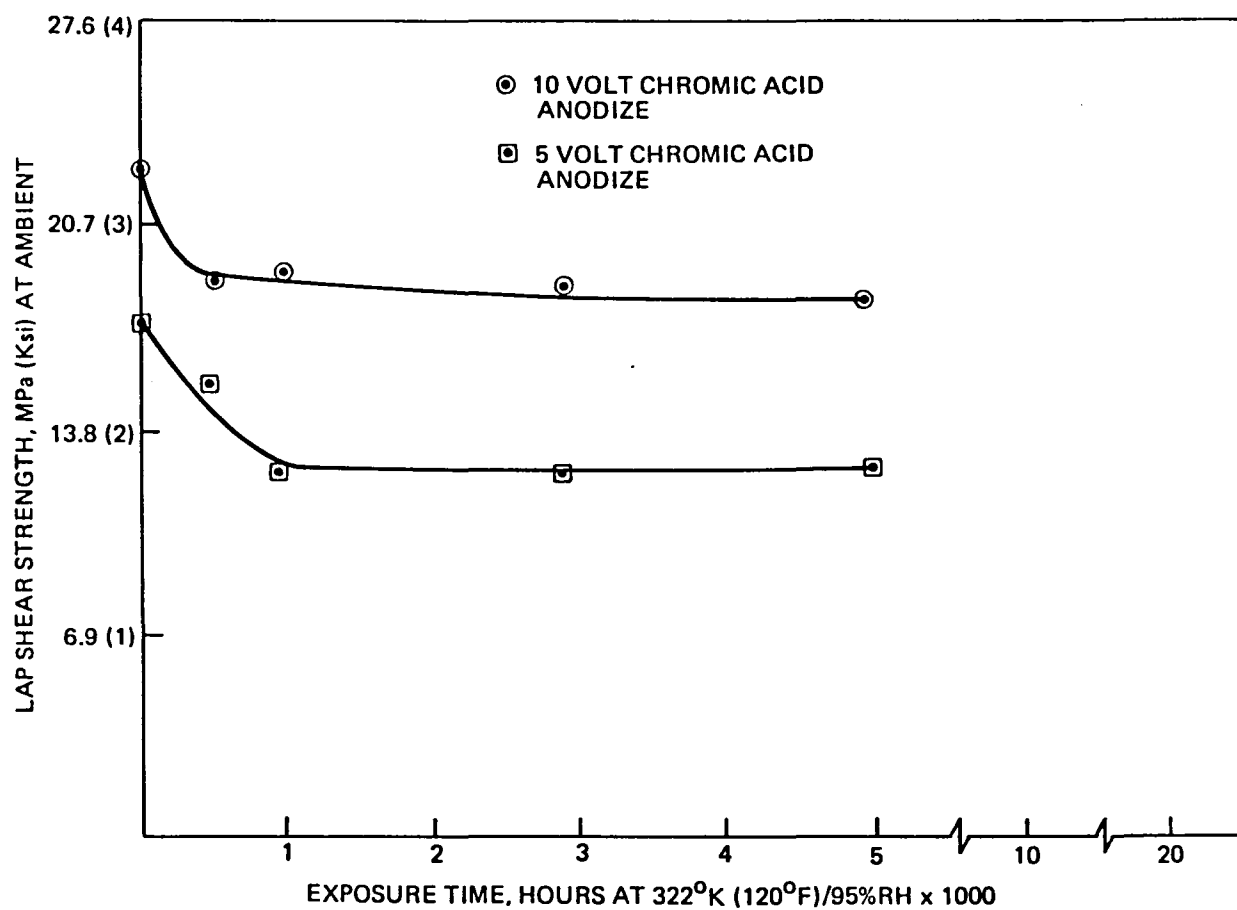


Figure 2.2-11:

NAS1-15605 SURFACE TREATMENT STUDY  
EFFECT OF 505°K (450°F) UPON ADHESIVE LAP SHEAR  
POLYPHENYLQUINOXALINE

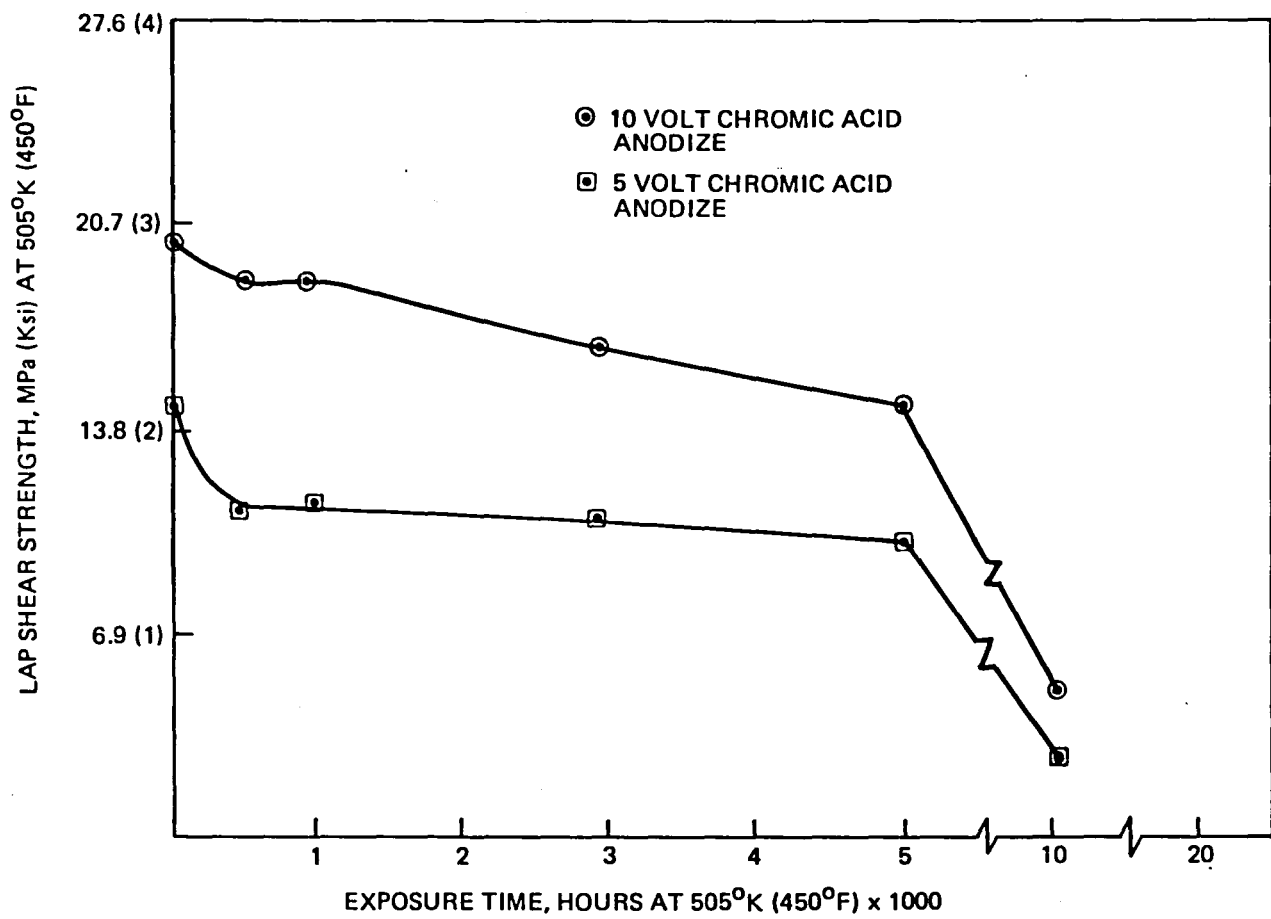


Figure 2.2-12:

Table 2.1-1. Summary Values, Titanium Surface Treatment Study—Lap-Shear Strength, MPa (psi)

		Exposure Time, hours						
Adhesive	Surface Preparation	Initial	500	1000	3000	5000	10,000	20,000
<u>322K (120°F)/100% RH, Ambient Test</u>								
LARC-13	10-V CAA	23.9 (3470)	21.1 (3060)	22.3 (3230)	19.3 (2890)	20.0 (2900)		
	Pasa-Jell	18.7 (2750)	16.9 (2490)	17.4 (2530)	17.4 (2520)	18.0 (2610)		
PPQ	10-V CAA	23.7 (3440)	18.7 (2710)	19.6 (2840)	17.7 (2570)	18.2 (2640)		
	5-V CAA	16.6 (2400)	14.6 (2120)	12.8 (1850)	12.6 (1820)	12.7 (1840)		
NR056X	10-V CAA	19.4 (2810)	17.0 (2460)	14.1 (2040)	16.1 (2330)	14.1 (2040)		
	Pasa-Jell	15.2 (2200)	7.8 (1130)	6.5 (940)	7.3 (1060)	6.5 (940)		
<u>505K (450°F) Exposure, 505K (450°F) Test</u>								
LARC-13	10-V CAA	20.1 (2920)	17.5 (2450)	13.5 (1960)	9.0 (1300)	6.8 (980)	2.4 (350)	TBD
	Pasa-Jell	18.8 (2770)	15.2 (2240)	12.1 (1760)	9.4 (1260)	7.5 (1090)	5.1 (740)	
PPQ	10-V CAA	20.2 (2930)	18.8 (2720)	19.0 (2750)	16.8 (2440)	15.4 (2240)	5.2 (750)	TBD
	5-V CAA	14.1 (2040)	11.2 (1630)	11.6 (1690)	11.3 (1640)	10.3 (1500)	3.8 (550)	
NR056X	10-V CAA	11.1 (1610)	11.2 (1630)	13.0 (1880)	11.1 (1610)	--- (1660)	7.9 (1140)	TBD
	Pasa-Jell	10.3 (1500)	7.8 (1130)	7.6 (1100)	6.4 (930)	--- (770)	3.0 (430)	

Table 2.1-2. Summary Values, Titanium Surface Treatment Study—Crack Extension, mm (in.)

Adhesive	Surface Preparation	Initial	Exposure Time, hours					
			500	1000	3000	5000	10,000	20,000
<u>322K (120°F)/100% RH Exposure</u>								
LARC-13	10-V CAA	31.0 (1.22)	4.6 (0.18)	6.3 (0.25)	7.4 (0.29)	7.4 (0.29)	9.4 (0.37)	TBD
	Pasa-Jell	37.6 (1.48)	10.6 (0.41)	13.2 (0.52)	15.2 (0.60)	16.0 (0.63)	18.0 (0.71)	
PPQ	10-V CAA	26.7 (1.05)	4.8 (0.19)	7.6 (0.30)	9.6 (0.38)	9.9 (0.39)	11.2 (0.44)	TBD
	5-V CAA	27.9 (1.10)	4.1 (0.16)	5.1 (0.20)	7.4 (0.29)	8.1 (0.32)	8.6 (0.34)	
NR056X	10-V CAA	28.2 (1.11)	8.1 (0.32)	9.4 (0.37)	13.2 (0.52)	19.0 (0.75)	20.3 (0.80)	TBD
	Pasa-Jell	34.0 (1.34)	6.6 (0.26)	7.4 (0.29)	9.6 (0.38)	13.0 (0.51)	13.7 (0.54)	
<u>505K (450°F) Exposure</u>								
LARC-13	10-V CAA	29.2 (1.15)	2.8 (0.11)	3.3 (0.13)	6.1 (0.24)	28.4 (1.12)	53.8 (2.12)	TBD
	Pasa-Jell	39.4 (1.55)	3.0 (0.12)	3.8 (0.15)	13.0 (0.51)	23.9 (0.94)	(Failed) 39.4 (1.55) (Failed)	
PPQ	10-V CAA	28.4 (1.12)	2.3 (0.09)	2.5 (0.10)	3.3 (0.13)	3.3 (0.13)	42.7 (1.68)	TBD
	5-V CAA	26.4 (1.04)	2.5 (0.10)	3.3 (0.13)	3.6 (0.14)	9.4 (0.37)	(Failed) 55.9 (2.20) (Failed)	
NR056X	10-V CAA	29.4 (1.16)	3.0 (0.12)	3.8 (0.15)	4.6 (0.18)	5.3 (0.21)	6.1 (0.24)	TBD
	Pasa-Jell	31.2 (1.23)	5.1 (0.20)	6.4 (0.25)	7.1 (0.28)	7.9 (0.31)	7.9 (0.31)	

Table 2.1-3. Surface Treatment Study—Lap-Shear Strength, MPa (psi),  
LARC-13 Exposure to 322K (120°F)/95% RH, Tested at Ambient

Initial	Exposure Time, hours			
	500	1000	3000	5000
<u>10-V CAA</u>				
24.3 (3520)	22.1 (3200)	23.2 (3360)	21.4 (3110)	21.6 (3130)
23.0 (3330)	17.1 (2480)	19.4 (2820)	15.6 (2270)	19.4 (2810)
23.4 (3400)	23.2 (3360)	23.7 (3440)	20.0 (2900)	20.3 (2940)
25.9 (3750)	20.7 (3000)	22.3 (3230)	22.1 (3210)	18.8 (2720)
23.0 (3330)	22.6 (3280)	22.7 (3290)	20.5 (2970)	20.0 (2900)
23.9 (3470) Avg.	21.1 (3060) Avg.	22.3 (3230) Avg.	19.3 (2890) Avg.	20.0 (2900) Avg.
<u>Pasn-Jell</u>				
15.9 (2320)	18.7 (2750)	16.9 (2450)	18.6 (2690)	16.4 (2380)
17.8 (2600)	18.0 (2640)	20.6 (2980)	18.0 (2610)	20.3 (2950)
17.9 (2630)	14.3 (2100)	15.4 (2230)	18.3 (2650)	17.2 (2490)
21.0 (3080)	18.6 (2740)	17.2 (2500)	15.2 (2210)	19.2 (2790)
21.3 (3130)	15.0 (2200)	16.5 (2390)	16.8 (2440)	16.7 (2420)
18.7 (2750) Avg.	16.9 (2490) Avg.	17.4 (2530) Avg.	17.4 (2520) Avg.	18.0 (2610) Avg.

Table 2.1-4. Titanium Surface Treatment Study—Lap-Shear Strength, MPa (psi),  
LARC-13 Exposure to 505K (450°F) Thermal Aging, Tested at 505K (450°F)

Initial	Exposure Time, hours					
	500	1000	3000	5000	10,000	20,000
<u>10-V CAA</u>						
17.7 (2570)	18.6 (2690)	12.4 (1800)	8.6 (1250)	5.4 (790)	3.8 (550)	TBD
19.3 (2800)	19.3 (2800)	13.4 (1950)	8.4 (1220)	8.1 (1180)	0.3 (40)	
21.0 (3050)	13.2 (1920)	14.2 (2060)	10.1 (1470)	7.8 (1130)	1.8 (260)	
21.6 (3130)	16.0 (2320)	12.9 (1870)	8.3 (1200)	5.6 (820)	2.1 (300)	
21.0 (3050)	17.5 (2540)	14.5 (2100)	9.4 (1360)	6.7 (970)	4.1 (600)	
20.1 (2920) Avg.	17.5 (2450) Avg.	13.5 (1960) Avg.	9.0 (1300) Avg.	6.8 (980) Avg.	2.4 (350) Avg.	
<u>Pasn-Jell</u>						
17.8 (2620)	12.9 (1900)	11.0 (1600)	8.3 (1200)	6.2 (900)	4.3 (620)	TBD
18.0 (2650)	15.0 (2200)	12.2 (1770)	8.5 (1230)	6.8 (990)	3.6 (530)	
18.0 (2640)	16.5 (2420)	12.3 (1780)	9.4 (1360)	8.3 (1200)	4.8 (700)	
20.2 (2970)	15.5 (2280)	12.6 (1820)	8.6 (1240)	8.0 (1160)	7.2 (1050)	
20.3 (2990)	16.3 (2400)	12.6 (1830)	8.9 (1290)	8.3 (1200)	5.6 (810)	
18.8 (2770) Avg.	15.2 (2240) Avg.	12.1 (1760) Avg.	9.4 (1260) Avg.	7.5 (1090) Avg.	5.1 (740) Avg.	

Table 2.1-5. Titanium Surface Treatment Study—Crack Extension, mm (in.)  
LARC-13 Exposure to 322K (120°F)/95% RH

Initial	Exposure Time, hours					
	500	1000	3000	5000	10,000	20,000
<u>10-V CAA</u>						
30.7 (1.21)	5.1 (0.20)	6.8 (0.27)	8.1 (0.32)	8.1 (0.32)	9.4 (0.37)	TBD
31.5 (1.24)	4.3 (0.17)	5.6 (0.22)	6.8 (0.27)	6.8 (0.27)	7.9 (0.31)	
30.7 (1.21)	5.1 (0.20)	7.4 (0.29)	8.1 (0.32)	8.1 (0.32)	10.9 (0.43)	
30.7 (1.21)	4.1 (0.16)	5.1 (0.20)	5.8 (0.23)	5.8 (0.23)	11.4 (0.45)	
31.0 (1.22) Avg.	4.6 (0.18) Avg.	6.3 (0.25) Avg.	7.4 (0.29) Avg.	7.4 (0.29) Avg.	9.4 (0.37) Avg.	
<u>Pusa-Jell</u>						
37.6 (1.48)	6.6 (0.26)	9.6 (0.38)	12.2 (0.48)	13.5 (0.53)	16.2 (0.64)	TBD
32.8 (1.29)	11.4 (0.45)	14.7 (0.58)	16.8 (0.66)	18.0 (0.71)	19.3 (0.76)	
43.2 (1.70)	11.9 (0.47)	15.2 (0.60)	17.8 (0.70)	17.8 (0.70)	19.3 (0.76)	
36.3 (1.43)	12.4 (0.49)	13.2 (0.52)	13.4 (0.55)	15.0 (0.59)	17.3 (0.68)	
37.6 (1.48) Avg.	10.6 (0.41) Avg.	13.2 (0.52) Avg.	15.2 (0.60) Avg.	16.0 (0.63) Avg.	18.0 (0.71) Avg.	

Table 2.1-6. Titanium Surface Treatment Study—Crack Extension, mm (in.)  
LARC-13 Exposure to 505K (450°F)

Initial	Exposure Time, hours					
	500	1000	3000	5000	10,000	20,000
<u>10-V CAA</u>						
29.2 (1.15)	3.8 (0.15)	3.8 (0.15)	6.6 (0.26)	24.6 (0.97)	53.8 (2.12)	Failed
29.0 (1.14)	2.8 (0.11)	2.8 (0.11)	10.7 (0.42)	28.4 (1.12)	53.8 (2.12)	Failed
3.3 (0.13)	4.1 (0.16)	30.2 (1.19)	54.6 (2.12) Failed		54.6 (2.15) Failed	
30.0 (1.18)	2.0 (0.08)	3.3 (0.13)	3.3 (0.13)	30.0 (1.18)	53.1 (2.09)	Failed
29.2 (1.15) Avg.	2.8 (0.11) Avg.	3.3 (0.13) Avg.	6.1 (0.24) Avg.	28.4 (1.12) Avg.	53.8 (2.12) Avg.	Failed
<u>Pusa-Jell</u>						
33.5 (1.32)	2.3 (0.09)	3.0 (0.12)	12.4 (0.49)	29.7 (1.17)	49.8 (1.96)	Failed
35.8 (1.41)	4.1 (0.16)	5.6 (0.22)	29.5 (1.16)	31.0 (1.22)	47.5 (1.87)	Failed
42.7 (1.68)	3.0 (0.12)	3.0 (0.12)	5.1 (0.20)	18.3 (0.72)	39.6 (1.56)	Failed
45.2 (1.78)	2.3 (0.09)	3.0 (0.12)	4.8 (0.19)	16.0 (0.63)	20.6 (0.81)	
39.4 (1.55) Avg.	3.0 (0.12) Avg.	3.8 (0.15) Avg.	13.0 (0.51) Avg.	23.9 (0.94) Avg.	39.4 (1.55) Avg.	

Table 2.1-7. Titanium Surface Treatment Study—Lap-Shear Strength, MPa (psi),  
PPQ Exposure to 322K (120°F)/95% RH, Tested at Ambient

Initial	Exposure Time, hours			
	500	1000	3000	5000
<u>10-V CAA</u>				
22.1 (3200)	18.3 (2650)	21.5 (3110)	20.0 (2900)	20.1 (2920)
22.2 (3220)	19.1 (2770)	20.1 (2920)	19.4 (2810)	19.9 (2880)
21.7 (3150)	18.1 (2620)	17.9 (2590)	19.6 (2850)	19.2 (2790)
25.5 (3700)	18.3 (2650)	18.2 (2640)	16.6 (2400)	14.0 (2030)
27.0 (3920)	19.6 (2850)	20.3 (2940)	19.3 (2800)	17.9 (2600)
23.7 (3440) Avg.	18.7 (2710) Avg.	19.6 (2840) Avg.	19.0 (2750) Avg.	18.2 (2640) Avg.
<u>Pasa-Jell</u>				
24.8 (3590)	18.2 (2640)	17.8 (2580)	18.2 (2640)	18.8 (2730)
14.2 (2060)	16.6 (2400)	13.4 (1940)	13.0 (1890)	12.3 (1780)
14.6 (2120)	16.8 (2430)	10.1 (1460)	8.3 (1210)	8.6 (1250)
13.4 (1940)	9.9 (1440)	8.3 (1200)	11.0 (1600)	11.6 (1690)
15.8 (2290)	11.6 (1690)	14.3 (2070)	12.1 (1750)	11.9 (1730)
16.6 (2400) Avg.	14.6 (2120) Avg.	12.8 (1850) Avg.	12.6 (1820) Avg.	12.7 (1840) Avg.

Table 2.1-8. Titanium Surface Treatment Study—Lap-Shear Strength, MPa (psi),  
PPQ Exposure to 505K (450°F), Tested at 505K (450°F)

Initial	Exposure Time, hours					
	500	1000	3000	5000	10,000	20,000
<u>10-V CAA</u>						
21.6 (3130)	15.4 (2240)	18.6 (2690)	16.8 (2430)	14.7 (2130)	4.6 (660)	TBD
20.6 (2980)	21.7 (3150)	20.8 (3020)	19.9 (2880)	16.4 (2380)	4.6 (670)	
18.1 (2620)	17.0 (2470)	18.8 (2730)	13.8 (2000)	18.3 (2660)	6.3 (910)	
19.9 (2880)	17.6 (2560)	20.5 (2970)	16.6 (2410)	14.6 (2120)	6.7 (970)	
21.0 (3040)	21.9 (3180)	16.0 (2320)	17.0 (2460)	13.0 (1890)	3.7 (530)	
20.2 (2930) Avg.	18.8 (2720) Avg.	19.0 (2750) Avg.	16.8 (2440) Avg.	15.4 (2240) Avg.	5.2 (750) Avg.	
<u>5-V CAA</u>						
18.5 (2680)	16.6 (2400)	16.3 (2360)	15.9 (2300)	13.3 (1930)	2.9 (420)	TBD
20.8 (3010)	14.0 (2030)	17.4 (2520)	14.2 (2060)	17.1 (2480)	2.7 (390)	
12.5 (1810)	9.9 (1440)	10.3 (1500)	11.9 (1720)	10.5 (1520)	5.0 (720)	
8.6 (1250)	7.6 (1110)	7.9 (1150)	7.7 (1120)	2.8 (400)	5.8 (840)	
9.9 (1440)	8.0 (1160)	6.3 (920)	6.9 (1000)	7.9 (1140)	2.5 (360)	
14.1 (2040) Avg.	11.2 (1630) Avg.	11.6 (1690) Avg.	11.3 (1640) Avg.	10.3 (1500) Avg.	3.8 (550) Avg.	

Table 2.1-9. Titanium Surface Treatment Study—Crack Extension, mm (in.),  
PPQ Exposure to 322K (120°F)/95% RH

Initial	Exposure Time, hours					
	500	1000	3000	5000	10,000	20,000
<u>10-V CAA</u>						
24.9 (0.98)	5.8 (0.23)	9.1 (0.36)	10.7 (0.42)	10.7 (0.42)	12.2 (0.48)	TBD
27.4 (1.08)	4.8 (0.19)	7.6 (0.30)	9.1 (0.36)	9.9 (0.39)	9.9 (0.39)	
27.2 (1.07)	3.3 (0.13)	6.6 (0.26)	8.6 (0.34)	8.6 (0.34)	11.2 (0.44)	
27.4 (1.08)	5.3 (0.21)	7.1 (0.28)	9.9 (0.39)	10.7 (0.42)	11.4 (0.45)	
26.7 (1.05) Avg.	4.8 (0.19) Avg.	7.6 (0.30) Avg.	9.6 (0.38) Avg.	9.9 (0.39) Avg.	11.2 (0.44) Avg.	
<u>5-V CAA</u>						
26.1 (1.03)	3.6 (0.14)	3.6 (0.14)	7.9 (0.31)	9.1 (0.36)	9.1 (0.36)	TBD
26.7 (1.05)	4.8 (0.19)	6.8 (0.27)	8.6 (0.34)	9.4 (0.37)	9.4 (0.37)	
29.5 (1.16)	3.6 (0.14)	3.6 (0.14)	4.8 (0.19)	4.8 (0.19)	4.8 (0.19)	
28.9 (1.14)	4.8 (0.19)	6.1 (0.24)	7.6 (0.30)	8.6 (0.34)	10.7 (0.42)	
27.9 (1.10) Avg.	4.1 (0.16) Avg.	5.1 (0.20) Avg.	7.4 (0.29) Avg.	8.1 (0.32) Avg.	8.6 (0.34) Avg.	

Table 2.1-10. Titanium Surface Treatment Study—Crack Extension, mm (in.),  
PPQ Exposure to 505K (450°F)

Initial	Exposure Time, hours					
	500	1000	3000	5000	10,000	20,000
<u>10-V CAA</u>						
27.4 (1.08)	2.8 (0.11)	2.8 (0.11)	4.1 (0.16)	4.1 (0.16)	45.2 (1.78)	TBD
27.9 (1.10)	2.5 (0.10)	3.6 (0.14)	3.6 (0.14)	3.6 (0.14)	35.3 (1.39)	
29.5 (1.16)	1.3 (0.05)	1.3 (0.05)	2.5 (0.10)	2.5 (0.10)	50.8 (2.00)	
29.5 (1.16)	2.5 (0.10)	2.5 (0.10)	2.5 (0.10)	2.5 (0.10)	37.3 (1.47)	
28.4 (1.12) Avg.	2.3 (0.09) Avg.	2.5 (0.10) Avg.	3.3 (0.13) Avg.	3.3 (0.13) Avg.	42.7 (1.68) Avg.	
<u>5-V CAA</u>						
26.9 (1.06)	1.8 (0.07)	2.5 (0.10)	2.5 (0.10)	2.5 (0.10)	54.6 (2.15)	TBD
25.9 (1.02)	3.8 (0.15)	4.3 (0.17)	5.3 (0.21)	5.3 (0.21)	56.6 (2.23)	
27.2 (1.07)	2.0 (0.08)	2.8 (0.11)	2.8 (0.11)	11.4 (0.45)	54.6 (2.15)	
25.9 (1.02)	3.0 (0.12)	3.0 (0.12)	3.0 (0.12)	18.3 (0.72)	57.1 (2.25)	
26.4 (1.04) Avg.	2.5 (0.10) Avg.	3.3 (0.13) Avg.	3.6 (0.14) Avg.	9.4 (0.37) Avg.	55.9 (2.20) Avg.	

Table 2.1-11. Titanium Surface Treatment Study--Lap-Shear Strength, MPa (psi),  
NR056X Exposure to 322K (120°F)/95% RH, Tested at Ambient

Initial	Exposure Time, hours			
	500	1000	3000	5000
<u>10-V CAA</u>				
22.3 (3240)	22.9 (3320)	13.8 (2000)	19.7 (2860)	18.8 (2730)
19.6 (2840)	15.0 (2180)	16.0 (2320)	20.9 (3030)	18.8 (2720)
23.4 (3390)	15.0 (2180)	12.4 (1800)	9.5 (1380)	9.6 (1400)
13.7 (1990)	14.6 (2110)	13.1 (1900)	16.1 (2340)	9.2 (1340)
17.9 (2600)	17.2 (2490)	15.3 (2220)	14.1 (2040)	13.7 (1990)
19.4 (2810) Avg.	17.0 (2460) Avg.	14.1 (2040) Avg.	16.1 (2330) Avg.	14.1 (2040) Avg.
<u>Pasa-Jell</u>				
15.1 (2190)	7.2 (1050)	6.8 (980)	9.6 (1400)	8.8 (1280)
11.5 (1670)	5.5 (800)	6.4 (930)	7.4 (1070)	3.0 (440)
14.8 (2140)	8.2 (1190)	6.7 (970)	8.8 (1280)	8.2 (1190)
22.3 (3240)	9.1 (1320)	5.9 (860)	5.1 (740)	7.4 (1070)
12.2 (1770)	9.1 (1320)	6.4 (930)	5.4 (790)	4.8 (700)
15.2 (2200) Avg.	7.8 (1130) Avg.	6.5 (940) Avg.	7.3 (1060) Avg.	6.5 (940) Avg.

Table 2.1-12. Titanium Surface Treatment Study--Lap-Shear Strength, MPa (psi),  
NR056X Exposure to 505K (450°F), Tested at 505K (450°F)

Initial	Exposure Time, hours					
	500	1000	3000	5000	10,000	20,000
<u>10-V CAA</u>						
11.6 (1680)	12.1 (1760)	12.9 (1870)	12.0 (1740)	8.7 (1260)	7.6 (1100)	TBD
11.4 (1660)	13.7 (1990)	14.5 (2100)	12.6 (1830)	14.3 (2080)	6.8 (990)	
7.6 (1100)	8.7 (1260)	12.4 (1800)	7.8 (1130)	9.4 (1360)	3.7 (540)	
11.0 (1600)	10.3 (1500)	13.3 (1930)	9.3 (1350)	9.4 (1360)	9.0 (1310)	
14.0 (2030)	11.0 (1590)	11.9 (1720)	13.9 (2020)	15.3 (2220)	12.1 (1760)	
11.1 (1610) Avg.	11.2 (1620) Avg.	13.0 (1880) Avg.	11.1 (1610) Avg.	11.4 (1660) Avg.	7.9 (1140) Avg.	
<u>Pasa-Jell</u>						
9.9 (1440)	6.9 (1000)	7.5 (1090)	6.8 (980)	5.5 (800)	3.6 (530)	TBD
8.1 (1180)	9.4 (1360)	6.3 (920)	7.4 (1070)	3.7 (540)	3.0 (440)	
11.0 (1600)	8.4 (1220)	8.6 (1240)	5.9 (860)	5.6 (820)	4.6 (660)	
11.6 (1690)	7.0 (1020)	8.6 (1250)	6.6 (950)	6.1 (880)	2.1 (310)	
11.1 (1610)	7.2 (1040)	7.0 (1020)	5.5 (800)	5.5 (800)	1.5 (220)	
10.3 (1500) Avg.	7.8 (1130) Avg.	7.6 (1100) Avg.	6.4 (930) Avg.	5.3 (770) Avg.	3.0 (430) Avg.	

Table 2.1-13. Titanium Surface Treatment Study—Crack Extension, mm (in.),  
NR056X Exposure to 322K (120°F)/95% RH

Initial	Exposure Time, hours					
	500	1000	3000	5000	10,000	20,000
<u>10-V CAA</u>						
27.7 (1.09)	9.1 (0.36)	11.2 (0.44)	14.2 (0.56)	TBD	TBD	TBD
27.9 (1.10)	8.1 (0.32)	9.9 (0.39)	12.4 (0.49)			
29.7 (1.17)	6.6 (0.26)	8.1 (0.32)	11.9 (0.47)			
27.2 (1.07)	8.4 (0.33)	8.4 (0.33)	14.7 (0.58)			
28.2 (1.11) Avg.	8.1 (0.32) Avg.	9.4 (0.37) Avg.	13.2 (0.52) Avg.			
<u>Pasa-Jell</u>						
33.5 (1.32)	6.1 (0.24)	7.4 (0.29)	9.1 (0.36)	TBD	TBD	TBD
37.6 (1.48)	5.3 (0.21)	5.3 (0.21)	7.4 (0.29)			
31.0 (1.22)	8.9 (0.35)	8.9 (0.35)	12.2 (0.48)			
34.0 (1.34)	5.8 (0.23)	7.6 (0.30)	10.2 (0.40)			
34.0 (1.34) Avg.	6.6 (0.26) Avg.	7.4 (0.29) Avg.	9.6 (0.38) Avg.			

Table 2.1-14. Titanium Surface Treatment Study—Crack Extension, mm (in.),  
NR056X Exposure to 505K (450°F)

Initial	Exposure Time, hours					
	500	1000	3000	5000	10,000	20,000
<u>10-V CAA</u>						
27.4 (1.08)	3.8 (0.15)	3.8 (0.15)	5.3 (0.21)	7.1 (0.28)	8.4 (0.33)	TBD
30.2 (1.19)	2.0 (0.08)	3.6 (0.14)	4.6 (0.18)	4.6 (0.18)	5.6 (0.22)	
29.4 (1.16)	2.5 (0.10)	3.8 (0.15)	4.8 (0.19)	4.8 (0.19)	4.6 (0.18)	
31.0 (1.22)	3.8 (0.15)	3.8 (0.15)	3.8 (0.15)	4.6 (0.18)	4.6 (0.18)	
29.4 (1.16) Avg.	3.0 (0.12) Avg.	3.8 (0.15) Avg.	4.6 (0.18) Avg.	5.3 (0.21) Avg.	6.1 (0.24) Avg.	
<u>Pasa-Jell</u>						
29.4 (1.16)	5.1 (0.20)	7.4 (0.29)	8.9 (0.35)	10.4 (0.41)	10.4 (0.41)	TBD
30.5 (1.20)	6.6 (0.26)	6.6 (0.26)	7.6 (0.30)	7.6 (0.30)	7.6 (0.30)	
33.3 (1.31)	4.6 (0.18)	5.8 (0.23)	5.8 (0.23)	7.1 (0.28)	7.1 (0.28)	
32.0 (1.26)	4.3 (0.17)	5.8 (0.23)	5.8 (0.23)	5.3 (0.23)	5.3 (0.23)	
31.2 (1.23) Avg.	5.1 (0.20) Avg.	6.4 (0.25) Avg.	7.1 (0.28) Avg.	7.9 (0.31) Avg.	7.9 (0.31) Avg.	

Long term thermal exposure to 505K (450°F) exhibited a change from cohesive to adhesive failure in lap shear between 5,000 and 10,000 hours.

Surface analysis of the adhesively failed lap shear coupons indicates fracture of the oxide as the primary cause of failure. This will be discussed in Section 2.1.4.

LARC-13 had experienced a relatively rapid drop in shear properties at 505K (450°F) from the initiation of exposure. These test results were the major factor for concluding that this resin is not stable at 505K (450°F) and would not meet the long term 20,000 hour strength objectives of the program. The fact that the surface oxide failed between 5,000 and 10,000 hours did not influence the overall decision that LARC-13 is no longer considered for the 505K (450°F) portion of this study. The oxide failure did reinforce a basic conclusion that the possible weak link at elevated temperature in all adhesive systems in evaluation is the anodize surface preparation.

#### 2.1.2 Analysis of NR056X Data

Long term 322K (120°F)/95% RH had slight effect upon crack growth in crack extension coupons (Figure 2.1-5). Exposure to 505K (450°F) had no effect upon crack extension (Figure 2.1-6), however, lap shear (Figure 2.1-8) dropped to very low values. Chromic acid anodize was clearly the superior surface treatment when compared to Pasqa Jell. As shown in Figure 2.1-8, the shear strength at 10,000 hours are far too low to be considered structural, especially since the objectives were to retain about 2,000 psi to 20,000 hours. The low mechanical strengths were, in part, due to oxide failure at 10,000 hours. Since DuPont has withdrawn this product from the market, NR056X cannot be considered for any further testing.

#### 2.1.3 Analysis of PPQ Data

As the long term exposure to both 322K (120°F)/95% RH (Figure 2.1-11) and 505K (450°F) (Figure 2.1-12) progressed it seemed that PPQ could possibly meet the 20,000 hour thermal stability requirements. Moisture exposure to 5,000 hours had little or no effect upon crack extension on lap shear strength and 505K (450°F) data to 5,000 hours was very good. However, the 10,000 hour values were very poor. Specimen failure changed from cohesive at 5,000 hours to 100% adhesive at 10,000 hours. Surface

analysis has shown again that failure is in the oxide layer. The almost uniform failure of the three adhesive systems in the oxide at 10,000 hour 505K (450°F) exposure presents a serious barrier to achieving desired structural bonds at 20,000 hours exposure for any adhesive resin. Apparently the resin stability exhibited by PPQ (for instance) cannot be adequately demonstrated as long as the potential for failure of the oxide exists.

Detailed discussion of the titanium surface structure created by various surface treatments and possible causes for failure in the anodize oxide when exposed to high temperature is presented in Section 2.1.4.

#### 2.1.4 Titanium Surface Analysis

##### Evaluation of Initial Prepared Surfaces

Titanium surface preparations evaluated in Phase I bonding studies were analyzed to better understand basic bond characteristics associated with high temperature stable adhesives. The objective of this effort is to correlate the surface morphology and composition of the different surface treatments with adhesive bond strengths. Adhesive bonds studied were LARC-13, NR056X, and polyphenylquinoxaline (PPQ). Surface preparations were divided into two groups:

- Anodization Methods
  - Chromic Acid Anodize (CAA)
  - Phosphoric Acid Anodize (PAA)

- Chemical Etch Methods
  - Turco 5578
  - Phosphate Fluoride (Picatinny Mod.)
  - Phosphate Fluoride
  - Pasa-Jell

The morphology of the surfaces studied were determined by:

- o Scanning Electron Microscopy (SEM) - for low resolution of a plan view.
- o Scanning Transmission Electron Microscope (STEM) - for high resolution of fractured-end-view.

- o Auger Electron Spectroscopy (AES) - for surface composition of top 50 angstroms and depth profiling to measure oxide thickness.

Figure 2.1.4-1 illustrates the comparison of oxide thickness with initial bond strength. NR056X was selected for this illustration. As shown, CAA has an oxide thickness of about 2500 angstroms compared to PAA with about 750 angstroms. The other surface preparations are all at about 250 angstroms thick. Lap shear strengths shown are proportional to the 29 MPa (4200 psi) CAA values. In general, it appears that increasing oxide thickness results in higher lap shear strengths.

Since the titanium alloy (6Al-4V) used as adherend has a significant amount of the other metal elements, analysis of the metal oxide chemistry was conducted in anticipation of other than pure titanium oxide on the surface. Figure 2.1.4-2 shows the atom percent of aluminum to titanium present in the oxide. The level of aluminum in the oxide was much higher than expected. As seen for CAA and PAA, the concentration of aluminum atoms to titanium atoms reaches about 0.65 and 0.50 respectively. Normal levels of aluminum based upon the alloy composition would be around 0.10 atom percent. The etch preparations also show high proportions of aluminum except Turco which produces only titanium oxide.

Some studies of titanium oxide surface used for bonding have indicated a correlation of fluorine concentration with bond strength (greater fluorine content reduces bond strength). Figure 2.1.4-3 shows the atom percent of fluorine found in the various surface oxides. PAA exhibited the highest fluorine content at about 0.33 atom percent while producing the second highest lap shear strengths. Turco 5578 did not yield any trace of fluorine. Based upon these results, no definite correlation of fluorine content (in the oxide) to lap shear strength was found.

The various surface treatments expose the adherend to other elements which are incorporated into the oxide. These elements are primarily silicon, sulfur, chlorine, calcium, iron, and copper. Figure 2.1.4-4 illustrates the total of other elements present in the oxide versus the lap shear strength. As shown, CAA and PAA are relatively "clean" oxides. The other four surfaces contain a relatively high proportion of these elements. General conclusions regarding this portion of the study would be that greater bond strengths are produced when stray elements are not present.

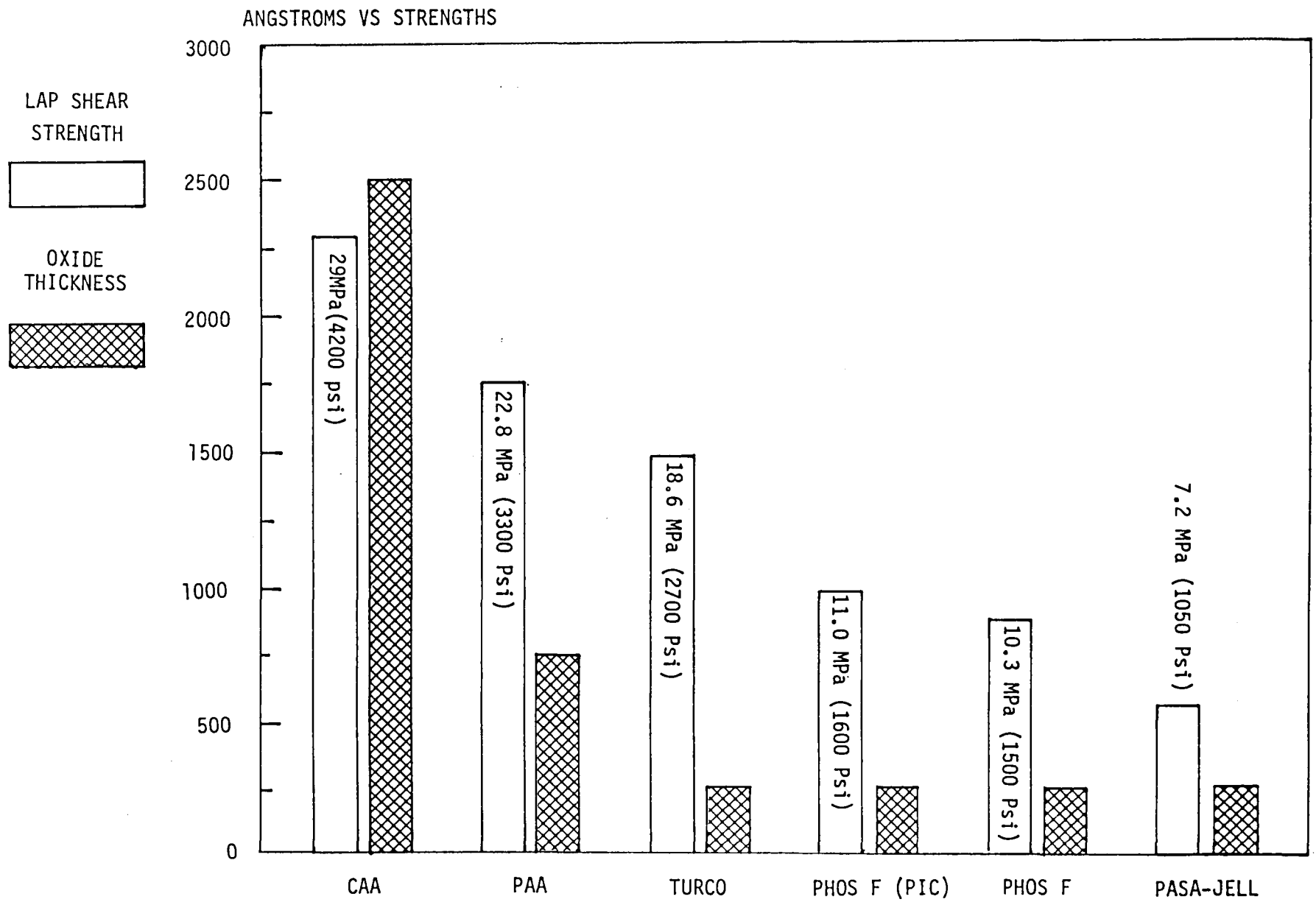


Figure 2.1.4-1 SURFACE TREATMENT OXIDE THICKNESS

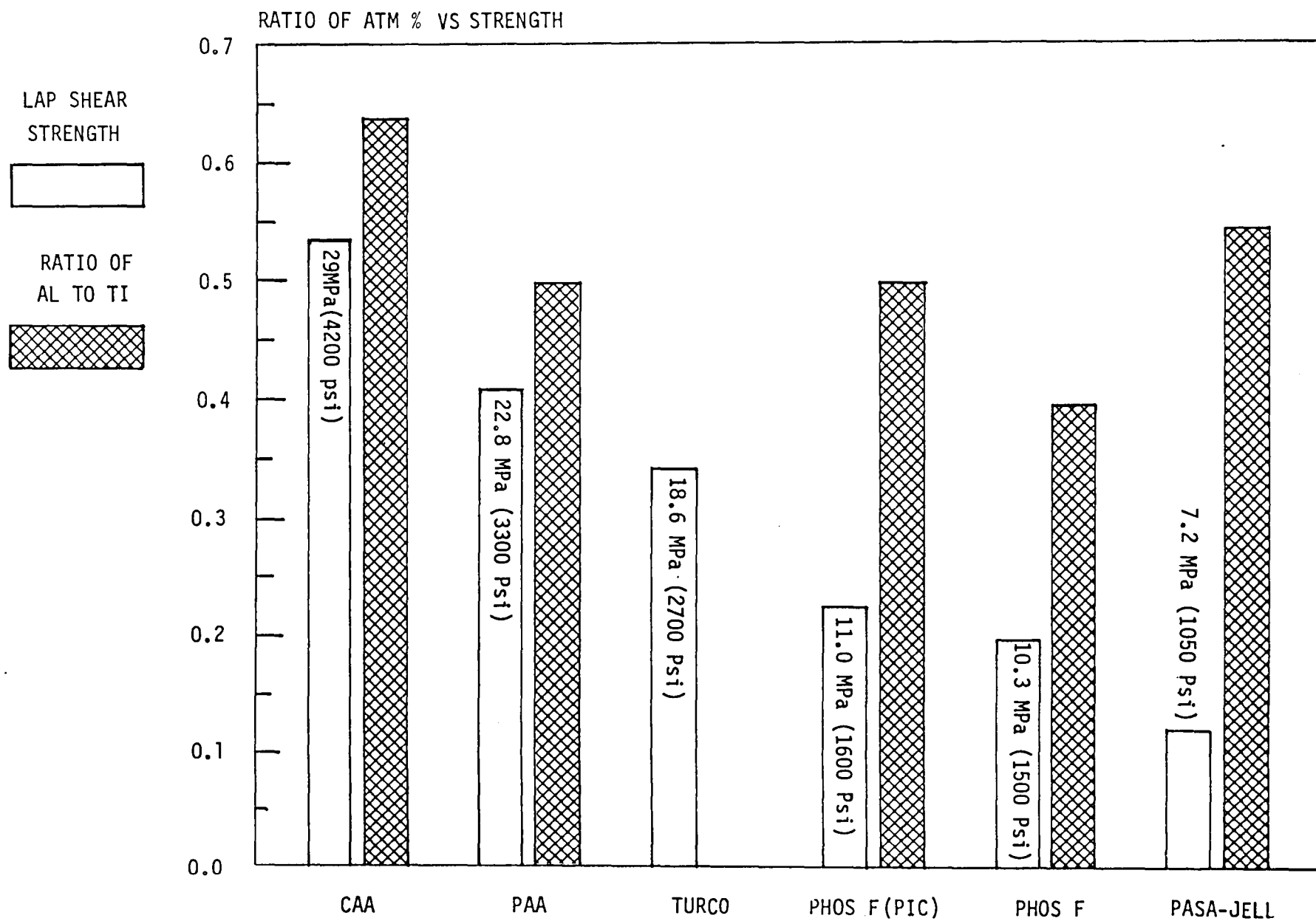


Figure 2.1.4-2 SURFACE TREATMENT AUGER ALUMINUM TO TITANIUM RATIO

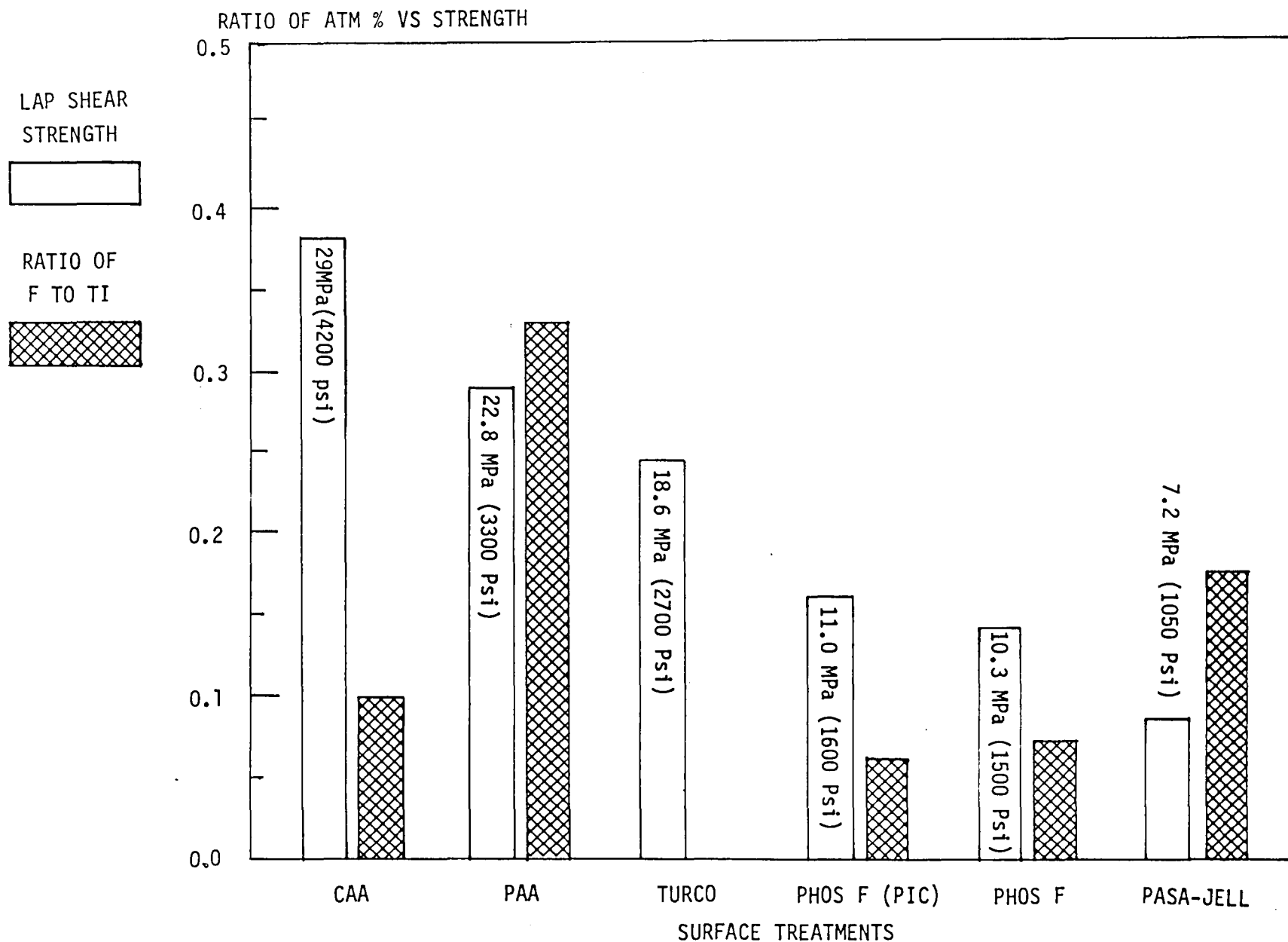


Figure 2.1.4-3 SURFACE TREATMENT AUGER FLUORINE TO TITANIUM RATIO

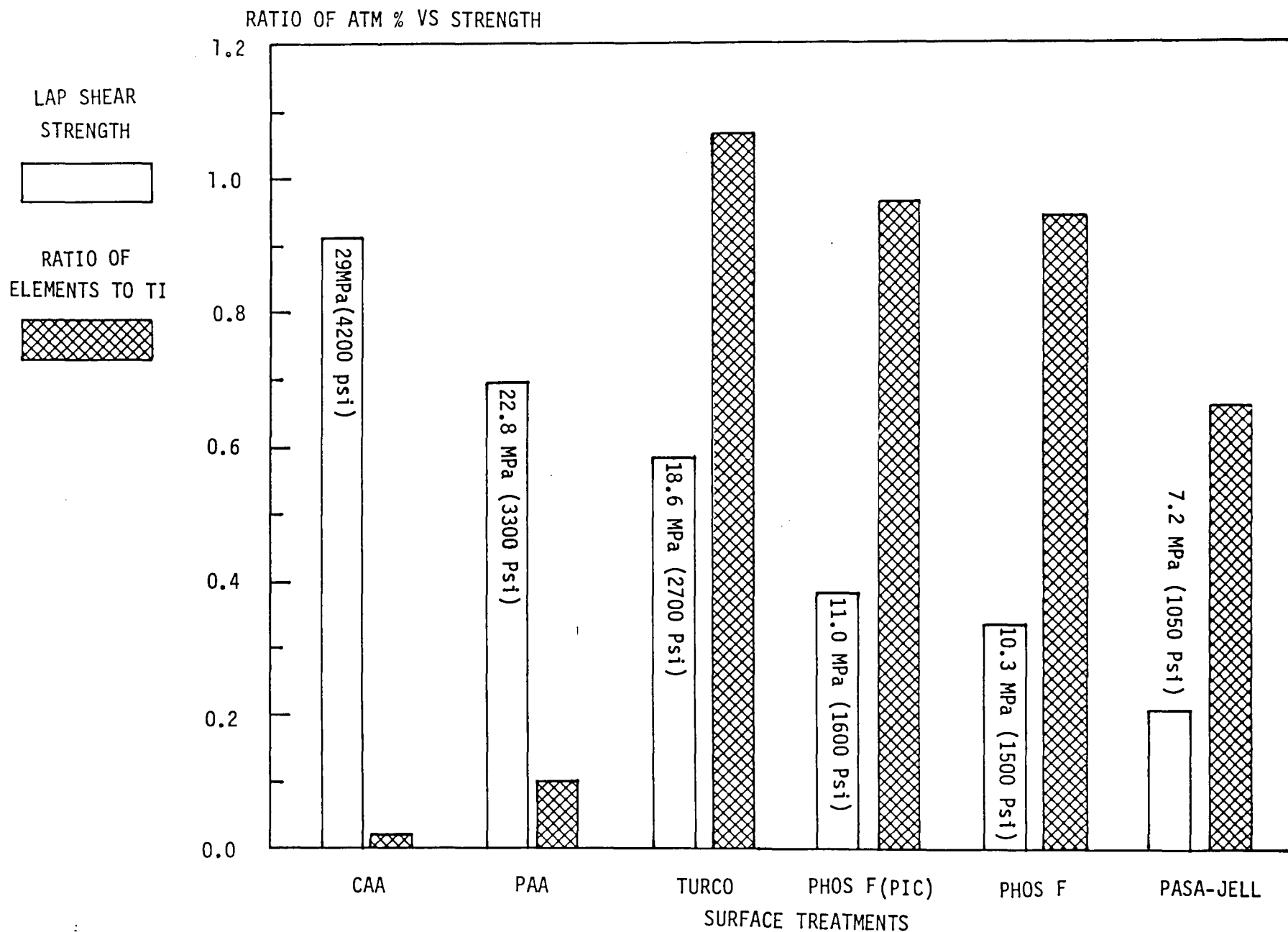


Figure 2.1.4-4 SURFACE TREATMENT REMAINING ELEMENTS TO TITANIUM RATIO

The conclusions reached with regard to oxide thickness and stray element contamination may not be independent of other variables, such as: oxide structure, etc.

#### Evaluation of Thermally Exposed Adhesive Failure Surfaces

The lap shear and crack extension coupons from Phase I long term thermal aging 505K (450°F) exhibited adhesive failures at the 10,000 hour test time. Previous failures of LARC-13 and PPQ during thermal aging were cohesive.

Surface analysis was performed by two methods, auger electron spectroscopy (AES) and electron spectroscopy for chemical analysis (ESCA). Both techniques can detect all elements above atomic number 2 within the top few monolayers on the examined surface, typically around 10 to 50 angstroms deep. The techniques differ in the means of sample excitation and in the type of electron emission detected.

AES utilizes an electron beam with a lateral resolution of .01 mm. The primary application of AES in this work is to map the elemental distribution across the failed lap shear surface. AES is severely effected by sample charging so it could only be used on the more electrically conductive adherend side.

ESCA is accomplished by excitation with magnesium K X-rays. It has a lateral resolution of approximately 5 mm in diameter. Unaffected by charging, ESCA was used to obtain an area-averaged elemental composition on the adhesive side of the failed lap-shear.

#### Polyphenylquinoxaline/10 Volt CAA

A low magnification photomicrograph of the adherend side of a failed lap-shear is shown in Figure 2.1.4-5. The light and dark areas indicated in the photo as Points A and B respectively, were analyzed by AES (see Figure 2.1.4-7). The light areas (Point A) have an elemental composition characteristic of the PPQ resin.

The darker areas (Point B) are high in titanium and oxygen indicating areas of oxide fracture. The presence of carbon is probably due to residual primer on the surface and/or contamination. Silicon, sulfur and chlorine were also detected in the 10V CAA baseline oxide characterizations reported in the third Semi-Annual Report to NASA on high temperature bond durability.

Figure 2.1.4-6 is a map of titanium concentration across the adherend surface shown in Figure 2.1.4-5. The roughly elliptical areas of oxide failure were observed to be directly below the scrim, while the surrounding areas of adhesive corresponds to the scrim nodes where there was a high degree of porosity.

ESCA spectra were taken on the adherend (Figure 2.1.4-8) and adhesive (Figure 2.1.4-9) to show that there is titanium oxide as well as PPQ on both sides of the lap-shear failure. The source of the lead, sulfur, and silicon have not been identified yet. ESCA is much more sensitive to lap lead than AES which accounts for lap. lead detection in ESCA only.

Figures 2.1.4-10 and 2.1.4-11 are scanning electron photomicrographs of the adhesive side of the PPQ/10V CAA failure which shows the oxide resides on the raised scrim areas. The smooth featureless appearance of the adhesive at the scrim nodes confirms the existence of bondline porosity ranging from 25 to 50% of the bonded area.

#### Polyphenylquinoxaline/5 Volt CAA

The photomicrograph of the adherend surface is shown in Figure 2.1.4-12. Again the light areas (Point A) were primarily PPQ adhesive and the dark areas (Point B) were areas of oxide failure. The AES spectra of Points A and B are included in Figure 2.1.4-14. A titanium map (Figure 2.1.4-13) reveals the same pattern of oxide failure seen in the PPQ/10V CAA lap shear failure. Visual examination confirmed that the elliptical areas of oxide failure were below the scrim and the interconnecting PPQ were below the scrim nodes.

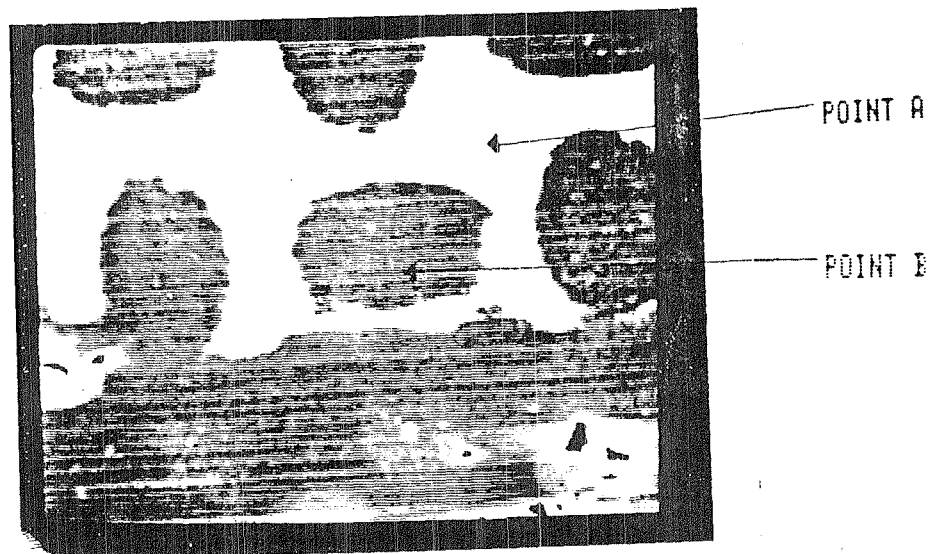


Figure 2.1.4-5 Absorbed Current Image (60X Magnification) Adherend Side of 10V CAA/PPQ Lap-Shear Thermal Exposure 10,000 Hours at 450°F.

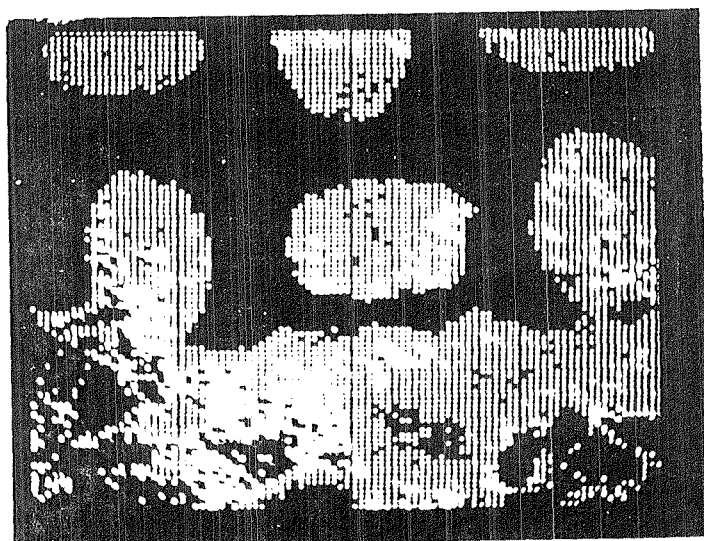


Figure 2.1.4-6 Titanium Auger Map of Figure 1, shows areas of Oxide Failure.

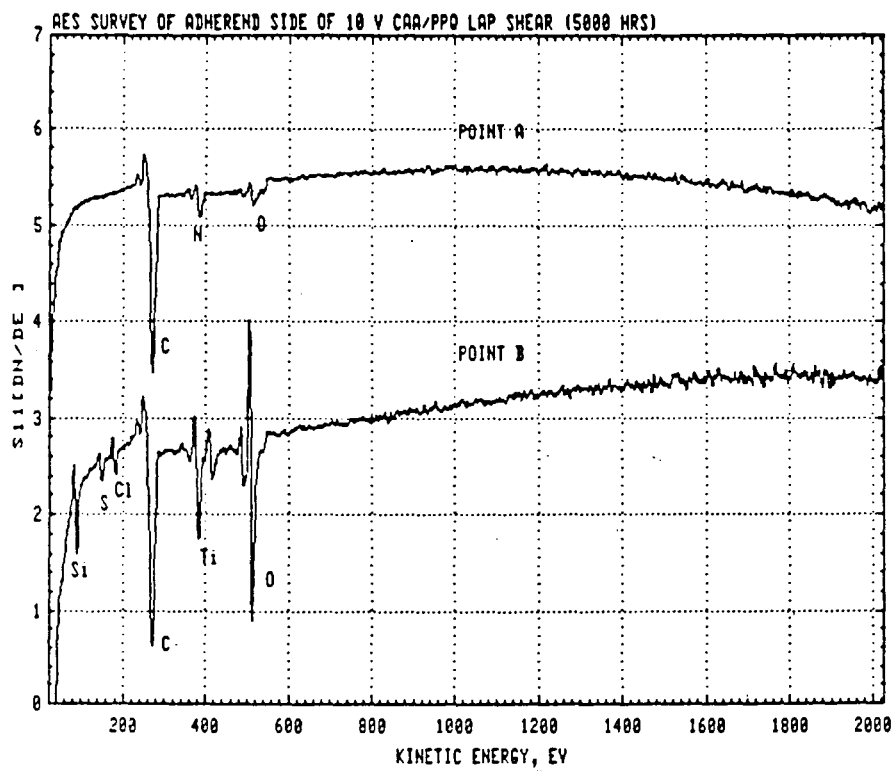


Figure 2.1.4-7 Auger Electron Spectra of Points A and B Shown in Figure 1.

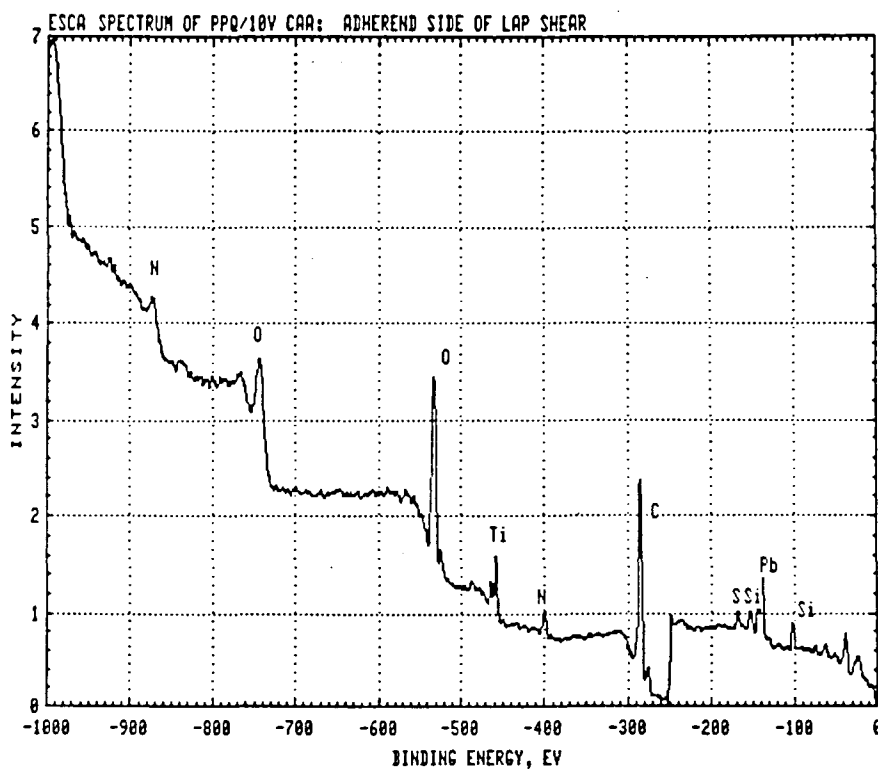


Figure 2.1.4-8 ESCA Spectrum of Adherend Side of 10V CAA/PPQ Lap-Shear Thermal Exposure 10,000 Hours at 450°F.

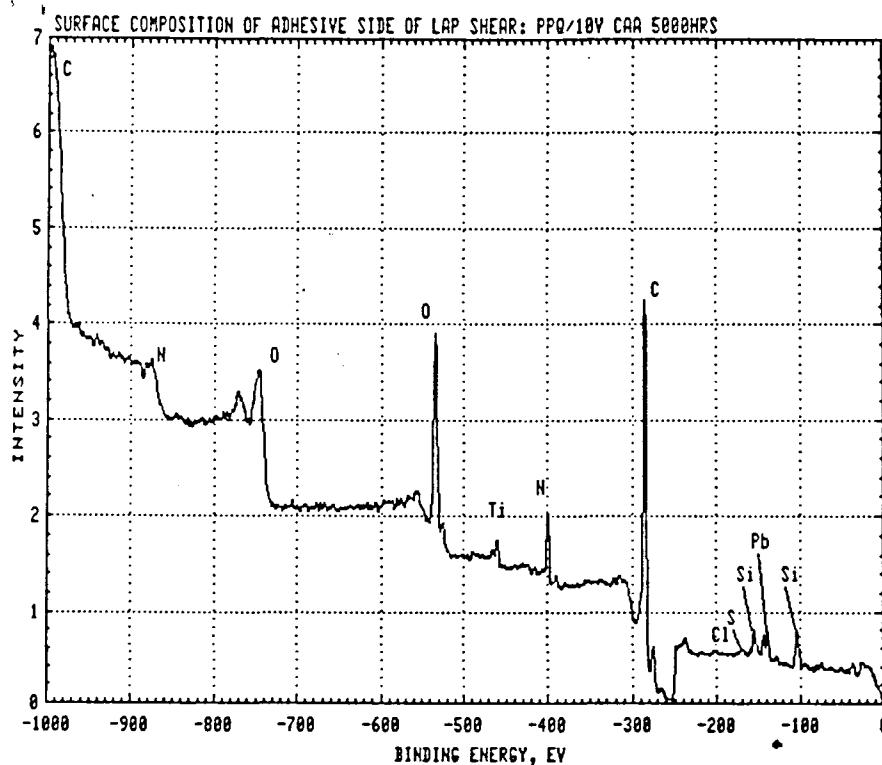


Figure 2.1.4-9 ESCA Spectrum Adhesive Side of 10V CAA/PPQ Lap-Shear Thermal Exposure 10,000 Hours at 450°F.

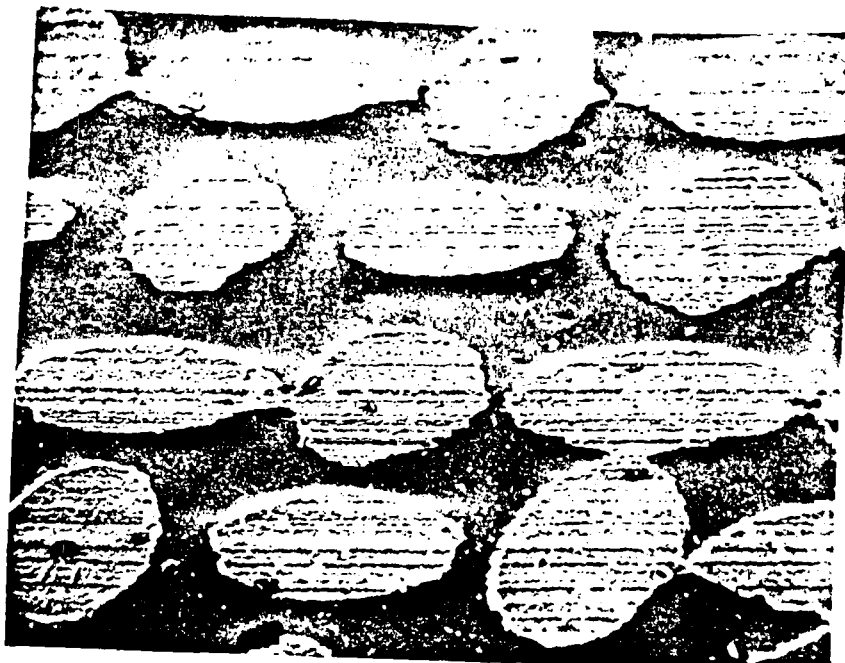


Figure 2.1.4-10 Scanning Electron Micrograph (Magnification 50X) Adhesive Side of 10V CAA/PPQ Lap-Shear shows elliptical islands of titanium oxide.

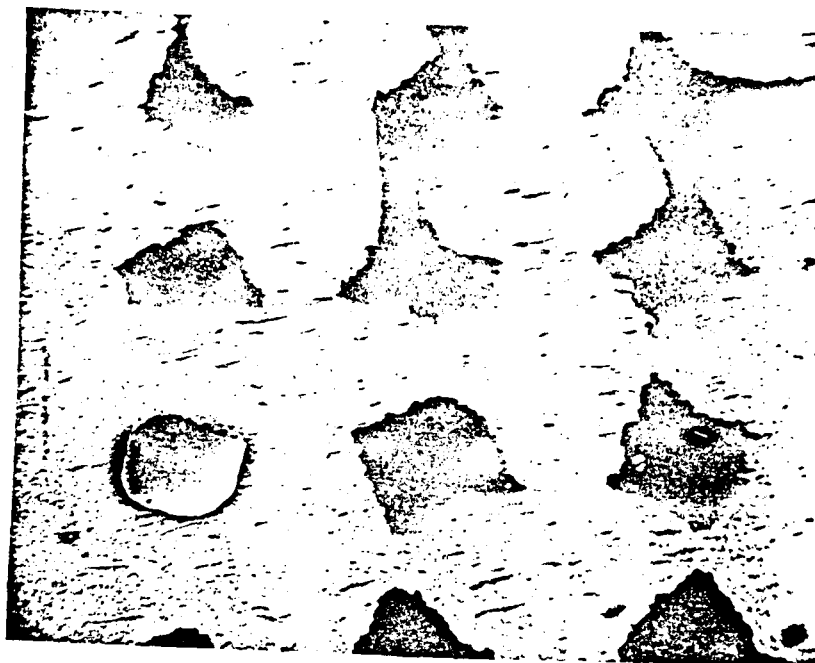


Figure 2.1.4-11 Scanning Electron Micrograph (magnification 50X) Adhesive side of 10V CAA/PPQ Lap-Shear shows larger areas of oxide.

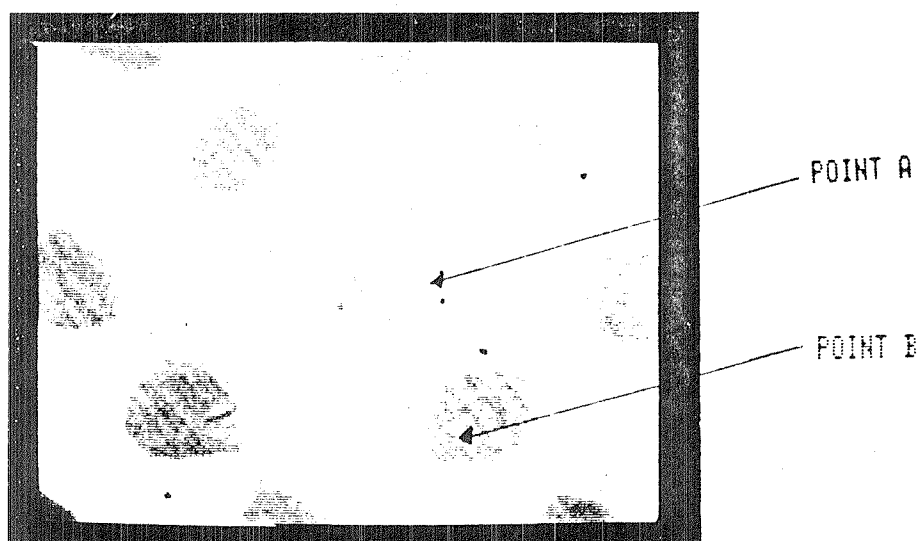


Figure 2.1.4-12 Absorbed current image (60X magnification) Adherend side of 5V CAA/PPQ Lap-shear thermal exposure 10,000 hours at 450°F.

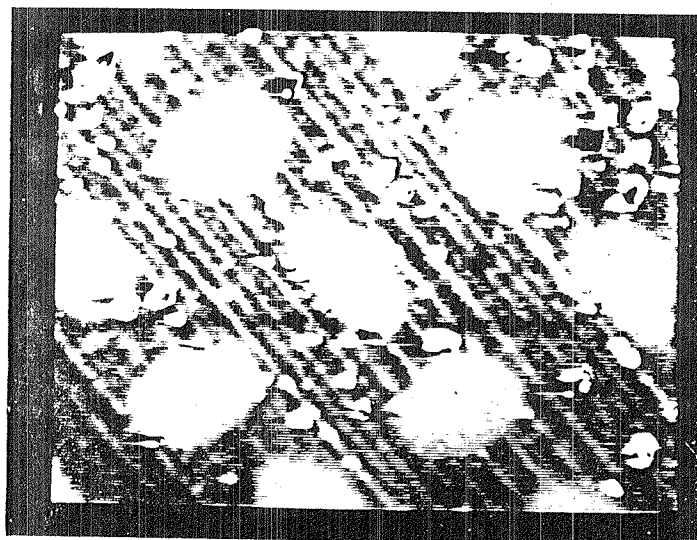


Figure 2.1.4-13 Titanium Auger Map of Figure 8, shows areas of oxide failure.

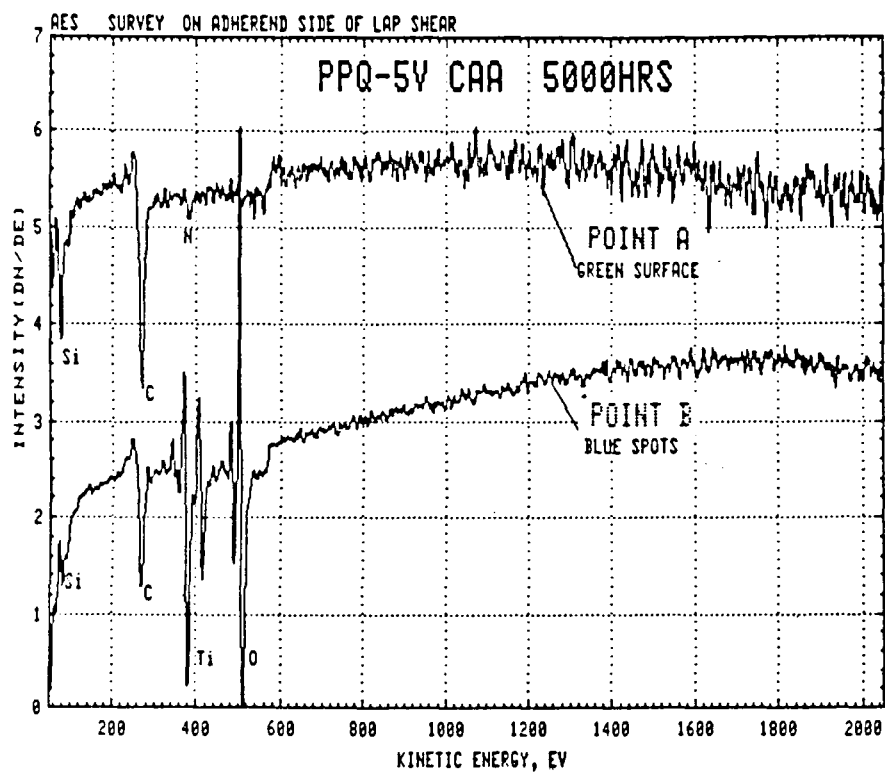


Figure 2.1.4-14 Auger Electron Spectra of Points A and B shown in Figure 8.

#### LARC-13/10 Volt CAA

A photomicrograph of the adherend side of the lap-shear is shown in Figure 2.1.4-15. The titanium map (Figure 2.1.4-16) indicates areas of oxide failure. The elemental composition (Figure 2.1.4-17) of the bare area (Point A) is primarily titanium oxide with lesser amounts of carbon and sulfur. The spectrum labeled Point B was taken in an area that was partly bare oxide and partly polymer covered to reduce the effects of severe charging encountered on the totally polymer areas. This spectrum also contains aluminum from the aluminum filler particles used in LARC-13.

#### LARC-13/Pasa-Jell

The photomicrograph of the adherend side of the lap-shear is shown in Figure 2.1.4-18. The elemental compositions (Figure 2.1.4-20 indicate that the bare areas (Point B) are areas of oxide failure and that there remains some LARC-13/Al filler particles in the areas labeled Point A.

Both adhesive systems exhibit oxide failures. However, the PPQ strengths-locus may be independent or appearance related to the scrim. This is because the PPQ scrim nodes contain voids which allow the crack to propagate up into the adhesive at the nodes during failure. The PPQ lap-shears with no thermal aging exhibited the same porosity yet failed cohesively. For this reason, it appears that porosity is not controlling the failure locus from thermal degradation of the bonded lap-shear. The LARC-13 specimens had a lesser amount of porosity. These specimens failed almost entirely at the oxide/polymer interface.

Previous surface characterization of the titanium surface preparations documented some key differences between 5V CAA, 10V CAA, and Pasa Jell. Both CAA oxides have an open porous structure which provide for adhesive penetration and increased bonding surface area. The 10V CAA oxide is approximately 15000 angstroms thick and the 5V CAA is 8000 angstroms thick.

In contrast, the Pasa-Jell oxide is only 100 angstroms thick with little or no open structure. Evidently, the LARC-13 lap-shear oxide failures are not influenced by large variations in oxide morphology represented by the 10V CAA and Pasa-Jell.



Figure 2.1.4-15 Absorbed current image (60X magnification) Adherend side of 10V CAA/LARC-13 Lap-shear thermal exposure 10,000 hours at 450°F.

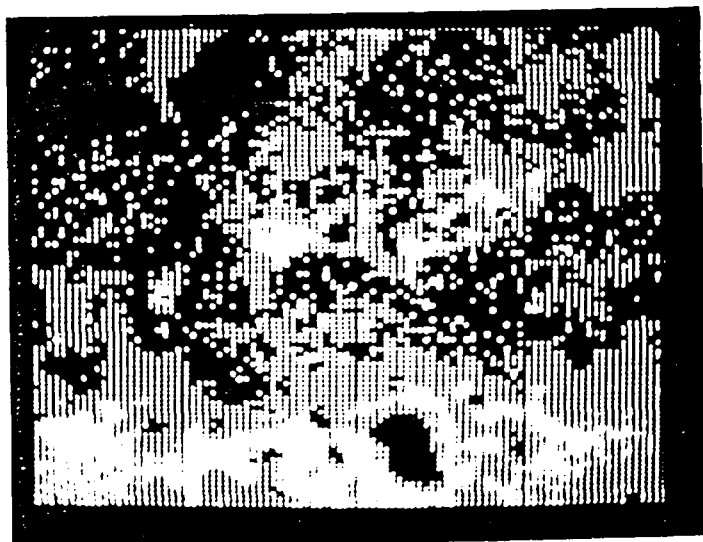


Figure 2.1.4-16 Titanium Auger map of Figure 11, shows areas of oxide failure.

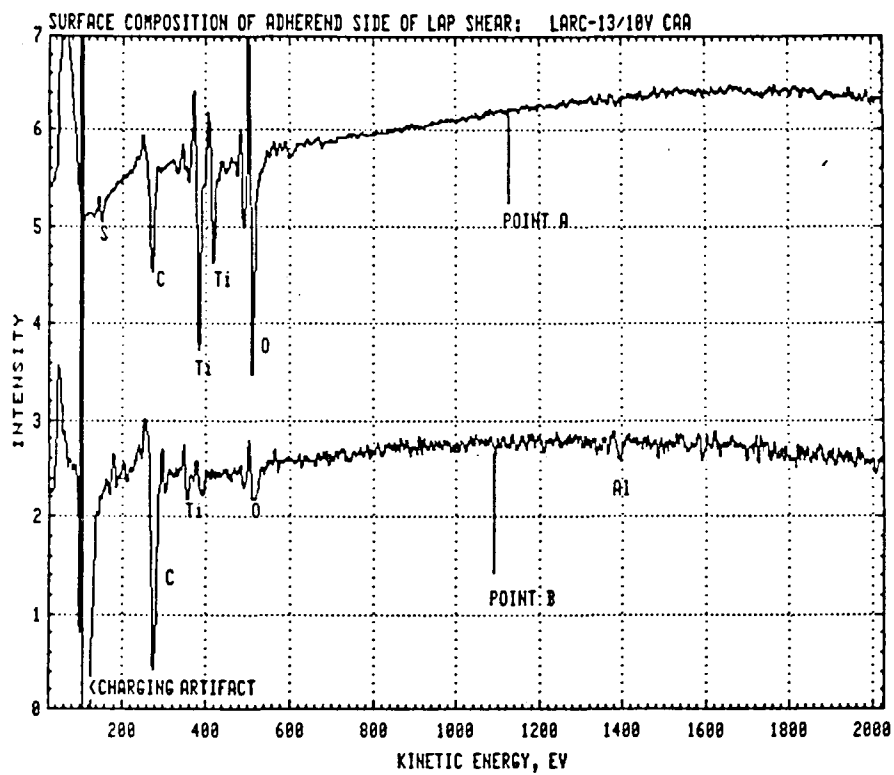


Figure 2.1.4-17 Auger electron spectra of points A and B shown in Figure 11.

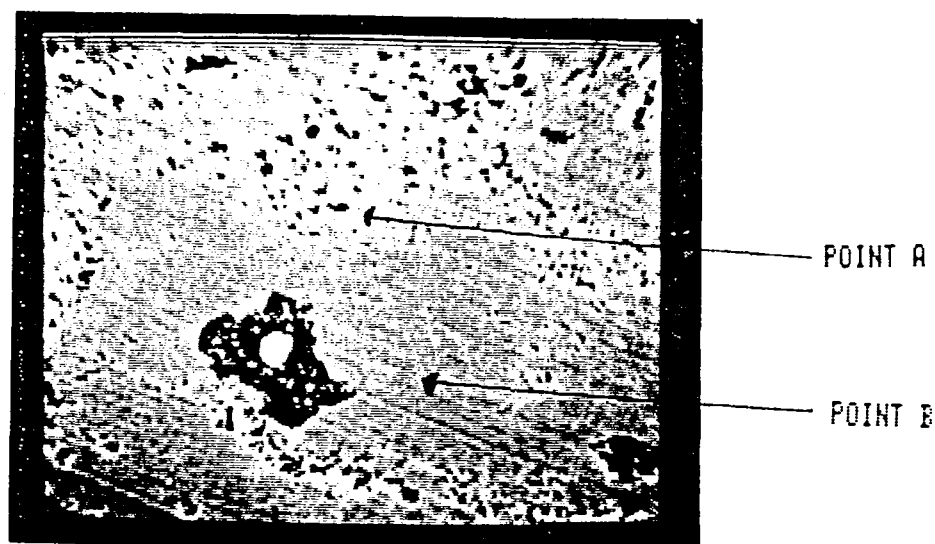


Figure 2.1.4-18 Absorbed current image (80X magnification) Adherend side of PASA JELL/LARC-13 Lap-shear Thermal Exposure 10,000 hours at 450°F.

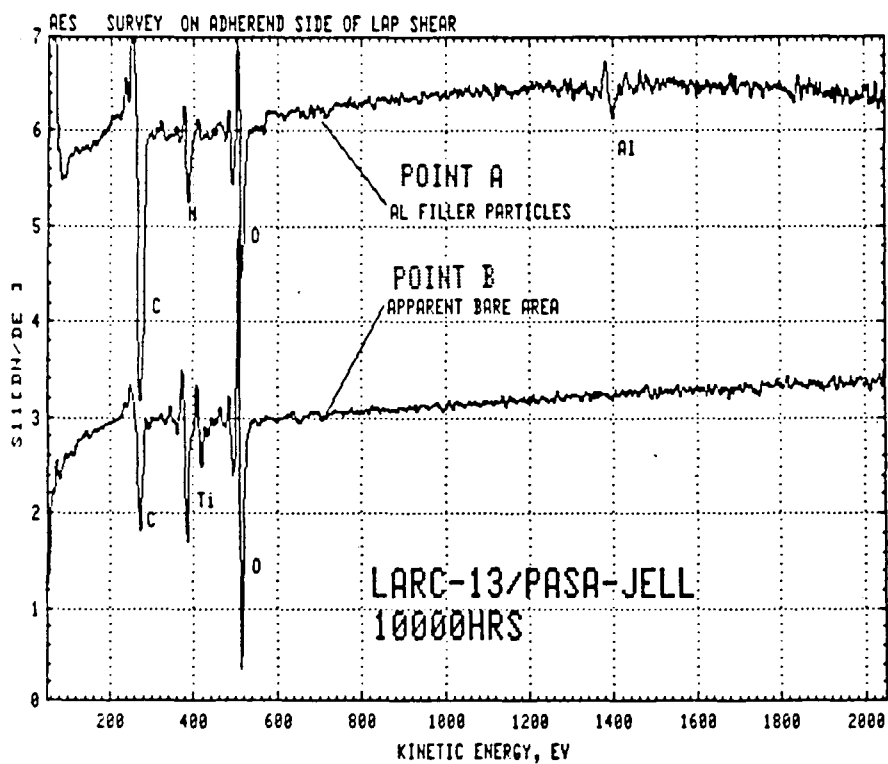


Figure 2.1.4-19 Auger electron spectra of points A and B shown in Figure 14.

It is useful to compare the PPQ and LARC-13 aging behavior to that of NR056X adhesive. NR056X lap-shears aged at 450°F for 10,000 hours failed cohesively. Thermal analysis of aged and unaged PPQ, LARC-13, and NR056X is included below.

GLASS TRANSITION TEMPERATURE OF ADHESIVES  
BEFORE AND AFTER EXPOSURE AT 450°F

PPQ	557°F
PPQ Exposed 10,000 Hrs	557°F
LARC-13	562°F
LARC-13 Exposed 5,000 Hrs	565°F
NR056X	648°F
NRO56X Exposed 5,000 Hrs	562°F

The lowering of the glass transition temperature for NR056X after thermal aging seems to indicate some degradation of the adhesive. This may account for the cohesive lap-shear failures even after thermal aging.

Summary

Thermally aged PPQ and LARC-13 lap-shears failed interfacially at or within the titanium oxide layer. Thermally aged NRO56X bonded lap-shears failed cohesively. The thermally aged PPQ and LARC-13 lap-shear oxide failures appear to be independent of titanium surface preparation, particularly in LARC-13 where there is a large variation in the oxide morphology between CAA and Pasa-Jell oxides.

The repeating pattern of oxide failure on the PPQ fracture surfaces is due to porosity at the scrim nodes, which reduces the effective bond area in the PPQ lap-shears.

High resolution scanning transmission electron microscopy will be used to determine the precise failure locus within the oxide. Further surface analysis studies will be performed on the oxide failures to determine if there is an interfacial segregating layer within the oxide.

## 2.2 PHASE II--ADHESIVE OPTIMIZATION AND CHARACTERIZATION

Phase II is divided into two separate tasks. Task I is an optimization and characterization study in which the two adhesives, PPQ and LARC-2, will be improved to standards required for production hardware quality and reliability. Task II will establish long-term environmental and durability data on the improved PPQ and LARC-2 systems.

### 2.2.1 Task I--Adhesive Optimization

#### Cure Cycle Optimization

Each of the adhesive systems is being evaluated for effect of various cure cycles upon adhesive properties. Description of the cure cycles used is found in the fourth semiannual report. Baseline data to 3,000 hours are presented in Table 2.2-1 through 2.2-4. Tests were conducted on only two of the five coupons for PPQ and LARC-13. The remainder will be tested after 10,000 hours of 450°F exposure to confirm the characteristic adhesive failures that have occurred previously at this aging time in Phase I surface treatment study test coupons.

#### Material and Process Specifications

Draft material and process specifications are included in the appendices of this report. The format for each is very similar to that currently used by Boeing. Each adhesive is treated as a different material (type) with corresponding requirements for chemical characterization, mechanical properties, and processing.

Table 2.2-1. Phase II Cure Cycle Optimization—Lap-Shear Strength, MPa (psi) Data Summary

Adhesive	Cure No.	Ambient Test	505K (450°F) Test	Thermal Aging at 505K (450°F) Tested at 505K (450°F)		
				500 hours	1000 hours	3000 hours
PPQ	1	30.2 (4380)	16.4* (2380)*	19.6 (2850)	20.8 (3010)	18.8 (2720)
	2	37.0 (5370)	17.4* (2530)*	24.4 (3540)	24.2 (3510)	24.8 (3600)
	3	33.0 (4780)	16.1* (2340)*	21.4 (3100)	22.9 (3320)	22.8 (3310)
LARC-2	1	19.9 (2880)	5.6* (810)*	14.8 (2140)	13.2 (1910)	15.6 (2260)
	2	19.3 (2800)	10.3 (1500)	13.0 (1890)	17.4 (2520)	16.6 (2400)
	3	27.6 (4000)	14.3 (2070)	15.6 (2260)	19.2 (2790)	19.7 (2860)
NR056X	1	21.2 (3080)	11.9 (1730)	13.4 (1950)	12.8 (1850)	9.7 (1410)
	2	20.7 (3000)	10.3 (1500)	10.8 (1570)	12.4 (1800)	10.2 (1480)
	3	21.5 (3120)	11.6 (1690)	13.0 (1890)	11.5 (1670)	12.1 (1750)

\*Oven temperature controller not functioning properly—test temperature exceeded 505K (450°F).

Table 2.2-2. Phase II Cure Cycle Optimization—PPQ—Lap-Shear Strength, MPa (psi)

Cure No.	Ambient Test, Initial	505K (450°F) Test, Initial	Thermal Aging at 505K (450°F) Tested at 505K (450°F)		
			500 hours	1000 hours	3000 hours
1	30.5 (4420)	17.7 (2570)	17.6 (2560)	20.8 (3020)	18.0 (2610)
	29.0 (4200)	13.9 (2020)	21.1 (3060)	17.0 (2470)	19.6 (2840)
	31.4 (4560)	17.1 (2480)	20.6 (2980)	21.5 (3130)	-- --
	32.1 (4660)	17.0 (2460)	19.0 (2760)	21.3 (3100)	-- --
	27.9 (4040)	16.3 (2360)	19.9 (2880)	23.1 (3350)	-- --
Average	30.2 (4380)	16.4 (2380)	19.6 (2850)	20.7 (3010)	18.8 (2720)
2	34.8 (5040)	17.0 (2460)	24.2 (3510)	24.9 (3610)	23.5 (3410)
	37.6 (5460)	16.2 (2350)	24.0 (3480)	23.4 (3400)	26.1 (3780)
	38.3 (5560)	17.6 (2550)	25.2 (3660)	22.6 (3280)	-- --
	38.8 (5620)	19.2 (2780)	23.9 (3470)	24.4 (3540)	-- --
	35.7 (5180)	17.4 (2530)	24.7 (3580)	25.5 (3700)	-- --
Average	37.0 (5370)	17.4 (2530)	24.4 (3540)	24.2 (3510)	24.8 (3600)
3	31.2 (4520)	13.8 (2000)	21.0 (3050)	21.7 (3150)	24.1 (3490)
	33.8 (4900)	17.8 (2580)	20.7 (3000)	21.6 (3140)	21.6 (3130)
	32.6 (4720)	17.0 (2470)	22.2 (3220)	24.3 (3530)	-- --
	34.6 (5020)	15.6 (2270)	18.3 (2660)	23.6 (3430)	-- --
	32.5 (4720)	16.3 (2370)	24.8 (3590)	23.1 (3360)	-- --
Average	33.0 (4780)	16.1 (2340)	21.4 (3100)	22.9 (3320)	22.8 (3310)

Table 2.2-3. Phase II Cure Cycle Optimization—LARC-2—Lap-Shear Strength, MPa (psi)

Cure No.	Ambient Test, Initial	505K (450°F) Test, Initial	Thermal Aging at 505K (450°F) Tested at 505K (450°F)		
			500 hours	1000 hours	3000 hours
1	19.9 (2880)	---	13.8 (2000)	13.9 (2010)	21.4 (3110)
	25.2 (3660)	---	15.0 (2180)	17.2 (2490)	9.8 (1420)
	16.6 (2400)	---	13.1 (1900)	7.8 (1130)	-- --
	18.5 (2680)	---	15.0 (2180)	13.2 (1920)	-- --
	19.3 (2800)	---	16.8 (2440)	13.9 (2010)	-- --
Average	19.9 (2880)	5.6 (810)	14.8 (2140)	13.2 (1910)	15.6 (2260)
2	16.8 (2440)	11.6 (1680)	13.0 (1890)	21.5 (3120)	21.8 (3160)
	15.0 (2180)	11.6 (1690)	11.0 (1600)	15.0 (2170)	11.3 (1640)
	19.6 (2840)	6.6 (950)	9.4 (1360)	23.6 (3430)	-- --
	26.2 (3800)	7.7 (1120)	12.3 (1780)	10.8 (1560)	-- --
	19.0 (2760)	14.1 (2040)	19.3 (2800)	15.9 (2300)	-- --
Average	19.3 (2800)	10.3 (1500)	13.0 (1890)	17.4 (2520)	16.6 (2400)
3	24.5 (3560)	14.7 (2130)	18.1 (2620)	18.7 (2710)	25.2 (3660)
	35.3 (5120)	14.9 (2160)	10.0 (1450)	18.5 (2680)	14.1 (2050)
	28.3 (4100)	15.6 (2260)	13.3 (1930)	25.7 (3730)	-- --
	19.9 (2880)	11.3 (1640)	22.1 (3200)	23.7 (3440)	-- --
	30.1 (4360)	14.8 (2150)	14.4 (2090)	9.9 (1440)	-- --
Average	27.6 (4000)	14.3 (2070)	15.6 (2260)	19.2 (2790)	19.7 (2860)

\*Temperature controller not operating properly, tested above 505K (450°F).

Table 2.2-4. Phase II Cure Cycle Optimization—NR056X—Lap-Shear Strength, MPa (psi)

Cure No.	Ambient Test, Initial	505K (450°F) Test, Initial	Thermal Aging at 505K (450°F) Tested at 505K (450°F)		
			500 hours	1000 hours	3000 hours
1	21.1 (3060)	13.0 (1880)	14.2 (2060)	14.1 (2040)	12.3 (1790)
	22.6 (3280)	11.6 (1690)	13.4 (1950)	12.4 (1800)	10.8 (1570)
	25.0 (3620)	11.6 (1680)	14.5 (2100)	11.2 (1620)	9.2 (1330)
	15.7 (2280)	13.4 (1940)	14.0 (2030)	12.7 (1840)	7.6 (1110)
	21.6 (3140)	10.2 (1480)	11.2 (1630)	13.3 (1930)	8.6 (1240)
Average	21.2 (3080)	11.9 (1730)	13.4 (1950)	12.8 (1850)	9.7 (1410)
2	20.0 (2900)	12.0 (1740)	8.4 (1220)	11.0 (1600)	12.4 (1800)
	22.2 (3220)	10.6 (1540)	13.0 (1880)	8.9 (1290)	10.1 (1470)
	17.2 (2500)	9.4 (1370)	8.8 (1280)	12.7 (1840)	10.6 (1540)
	23.0 (3340)	6.6 (960)	12.8 (1860)	15.7 (2280)	9.2 (1330)
	21.0 (3040)	13.0 (1890)	11.2 (1620)	13.7 (1990)	8.6 (1240)
Average	20.7 (3000)	10.3 (1500)	10.8 (1570)	12.4 (1800)	10.2 (1480)
3	21.9 (3180)	12.1 (1760)	11.8 (1710)	10.8 (1560)	15.4 (2240)
	22.6 (3280)	10.3 (1500)	9.9 (1430)	11.9 (1730)	13.9 (2020)
	24.1 (3500)	9.3 (1350)	15.0 (2170)	11.1 (1610)	8.6 (1240)
	18.6 (2700)	13.1 (1900)	13.0 (1890)	9.8 (1420)	11.4 (1660)
	20.1 (2920)	13.5 (1960)	15.6 (2260)	13.9 (2020)	10.8 (1570)
Average	21.5 (3120)	11.6 (1690)	13.0 (1890)	11.5 (1670)	12.1 (1750)

### Chemical Characterization

The objective of this portion of the program is to characterize each of the three adhesives and determine (from the analysis of three resin batches of each adhesive) the batch-to-batch variation. Resin batches analyzed to data are identified as follows:

<u>Resin</u>	<u>Resin Batch Number</u>	<u>Identification Code</u>
PPQ	PH 813-88	P-1
PPQ	NAS1-15605-2	P-2
PPQ	NAS1-15605-3	P-3
LARC-13	NAS1-15644	L-1
LARC-13	REF-RE-816-8	L-2
LARC-13	BAC 10-13-80 synthesis	L-3
NR056X	E17602-152-1	N-1
NR056X	E17602-152-2	N-2
NR056X	E17602-152-3	N-3

The chemical/physical tests and instruments used for analysis are as follows:

- o Infrared analysis--Digilab 15A Fourier Transform IR
- o Thermogravimetric analysis--DuPont 990 Thermal Analyzer
- o Liquid chromatography--DuPont 850 and Varian 5000
- o Differential scanning calorimetry--DuPont 990

Data charts for all analyses are attached as part of the appendices.

- o Polyphenylquinoxaline Analysis

The individual batches of PPQ were purified by diluting the original solution with chloroform. PPQ resin was then precipitated in methanol and separated by filtration. The resin precipitate was redissolved in methanol, boiled for 30 minutes, and refiltered. The precipitate was then dried at 100°C under vacuum.

Infrared Analysis--Resin samples were prepared by evaporating a resin film to a salt block surface. Analysis was performed on a Digilab 15A Fourier Transform spectroscopy unit. The typical spectra of each batch were almost identical.

Thermal Gravimetric Analysis--Each of the PPQ batches were 16% resin content from the weight loss curves. Analysis was conducted on a DuPont 990 Thermal Analyzer. Heatup rate was 5°C/minute with an air flow rate of 200 ml/minute. The sample weight was recorded on each analysis and the weight loss recorded directly in percent. Thermal degradation initiated at 560°C for each of the resin batches.

Liquid Chromatography--Liquid chromatography analysis of the PPQ resin batches was conducted almost entirely using size-exclusion chromatography techniques. Two columns were used: PSM 60S and PSM 1000S from DuPont. The mobile phase used for PPQ was chloroform. The detector was set at 254 nm and 280 nm. The three resin batches were all identical, with a single peak at 433 nm for P-1 and P-2 and 431 nm for P-3.

Differential Scanning Calorimetry--The PPQ resin samples were first heated to 325°C to remove excess solvent, then quick quenched in liquid nitrogen. The quenched samples were analyzed on a DuPont 990 thermal analyzer. Heatup rate was 20°C/minute. The DTA curve for each resin batch exhibited an endotherm at 300°C followed by an exotherm proceeding to the 380°C upper heating limit.

o LARC-13 Analysis

The various analyses were conducted on the resin portion only. A sample of each resin batch was centrifuged to separate solid fillers from the resin solution.

Infrared Analysis--Resin from each of the batches was cast on a salt block for analysis. Infrared scans of the resin films exhibited no apparent differences in the absorption spectra.

Thermal Gravimetric Analysis--The thermal profile of LARC-13 occurred in three steps; the first was apparently lower boiling solvent (dimethyl formamide) and the second weight loss was the result of condensation reaction volatiles. Rapid thermal

degradation occurred at 540-550°C. Direct comparison to the PPQ TGA curves would indicate the relative lack of thermal stability by LARC-13.

Liquid Chromatography--For this analysis (size-exclusion chromatography), two columns were used: PSM 60S and PSM 1000S. Methanol was used for the mobile phase. The three LARC-13 samples exhibited good consistency with four definite elution bands:

<u>Elution Time, minutes</u>	<u>Percent Absorption</u>
734	14.1
765	24.0
812	61.9

The fourth peak (band) was not computed by the integrator. In addition to size-exclusion chromatography, preliminary work was accomplished using partition and absorption chromatography. Both of these techniques resulted in detailed spectra that would take considerable effort to standardize for quality control requirements. Size-exclusion chromatography is the superior method of analysis for future quality control requirements.

Differential Scanning Calorimetry (DSC)/Differential Thermal Analysis (DTA)--LARC-13 DSC/DTA exhibited a broad endotherm between 150 and 225°C with strongest activity at about 200°C. Exotherm response was very slight at about 325 and 350°C. Some batch-to-batch variation was seen in this analysis that may be related to the original volatile content of the individual resin samples.

o NR056X Analysis

The analyses were conducted on the resin portion only. Fillers and/or other solid materials were centrifuged to obtain relatively pure resin solutions.

Infrared Analysis--Resin from each of the batches was cast on a salt block surface for analysis. Each of the three batches produced spectra with no detectable differences.

Thermal Gravimetric Analysis--NR056X exhibited a three-stage breakdown. The first two weight losses were attributed to solvent evaporation. Thermal degradation began at about 450°C for each batch.

Liquid Chromatography--Size-exclusion chromatography was conducted identically to that for LARC-13 with PSM 60S and PSM 1000S columns and methanol mobile phase. NR056X did show considerable variation in formulation. The data below illustrate these differences.

<u>Batch N-1</u>		<u>Batch N-2</u>		<u>Batch N-3</u>	
<u>Elution</u> <u>Time,</u> <u>minutes</u>	<u>Percent</u> <u>Area</u>	<u>Elution</u> <u>Time,</u> <u>minutes</u>	<u>Percent</u> <u>Area</u>	<u>Elution</u> <u>Time,</u> <u>minutes</u>	<u>Percent</u> <u>Area</u>
409	56.0	405	20.2	407	28.9
581	2.3	606	3.1	603	0.9
600	2.8	642	0.6	645	0.5
673	38.9	682	76.1	678	69.7

For this specific study, size-exclusion chromatography could give sufficient characterization for quality control.

Differential Scanning Calorimetry (DSC)/Differential Thermal Analysis (DTA)--The analysis of NR056X (for the three resin batches) exhibited a significant exotherm at 130 to 175°C followed by an exotherm event that took place between 225 and 325°C. Heatup rate for analysis was 10°C per minute. Sample size was 11.5 mg.

#### Conclusion

PPQ--The various analyses performed show excellent consistency among the three resin batches. Variation of test data would not be attributed to resin inconsistencies.

LARC-13--Reasonably good consistency in batch characteristics is maintained. Variations among the batches seem to lie in the amounts of volatiles and solvents

present. The relative lack of thermal stability is a cause of some concern in consistency of thermal aging tests.

NR056X—Formulation variations among the batches seem to be significant for this resin. DSC and DTA results also show a wide range of endotherm and exotherm temperatures. To characterize the resin, IR analysis, TGA, and size-exclusion chromatography could be effectively used.

### **2.2.2 Task II—Environmental Exposure Data**

This task is obtaining experimental data on PPQ and LARC-2 adhesive systems. Details of the different exposure tests are reviewed to clarify the present planned activities of this task.

#### **Unstressed Thermal Aging**

Lap-shear, T-peel, and crack-extension specimens are in the process of thermal aging at 450°F for 5,000 hours. At time intervals of 100; 500; 1,000; and 2,000 hours, five lap-shear specimens and five T-peel specimens were removed and tested for residual strength. Test determinations were made at -65, ambient, +300, and +450°F. At the same time intervals, the crack-extension specimens were examined, the crack length measured and recorded, and the specimens replaced for further aging. This study requires the fabrication and testing of 100 lap-shear, 100 T-peel, and five crack-extension specimens for each of the two systems. The data generated on PPQ is presented in Tables 2.2-5, 2.2-6, 2.2-7, and 2.2-8.

#### **Stressed Thermal Aging**

These tests are designed to facilitate the prediction of 50,000-hour service at 450°F by exposing lap-shear specimens under load for varying periods of time and then testing for residual strength. From these data, a plot of residual strength versus time will be made for each stress level and temperature tested. From the trends, a prediction of long-term performance will be attempted.

Table 2.2-5 Unstressed Thermal Aging, PPQ

## Data Summary

Test Coupon	Test Temperature K (°F)	Exposure Time				
		Initial	100 hours	500 hours	1000 hours	2000 hours
Lap Shear, MPa (psi)	219 (-65)	33.2 (4810)	34.9 (5060)	33.1 (4800)	30.3 (4390)	26.7 (3870)
	Ambient	32.3 (4680)	32.3 (4690)	34.3 (4970)	32.5 (4710)	23.7 (3440)
	422 (300)	25.2 (3660)	23.7 (3430)	25.4 (3690)	26.8 (3890)	23.3 (3380)
	505 (450)	20.5 (2970)	20.8 (3010)	22.6 (3270)	25.4 (3680)	21.1 (3060)
	533 (500)	15.2 (2200)	--	--	--	--
T-Peel, N·M (lb/in.)	219 (-65)	0.67 (5.9)	0.61 (5.4)	0.62 (5.5)	0.68 (6.0)	0.49 (4.3)
	Ambient	0.60 (5.3)	0.62 (5.5)	0.64 (5.7)	0.66 (5.8)	0.51 (4.5)
	422 (300)	0.79 (7.0)	0.69 (6.1)	0.61 (5.4)	0.75 (6.6)	0.45 (4.0)
	505 (450)	0.91 (8.1)	0.74 (6.6)	0.74 (6.6)	0.77 (6.8)	0.76 (6.7)
	533 (500)	0.90 (8.0)	--	--	--	--
Crack Extension, mm (inches) growth	219 (-65)	1.0 (0.04)	1.0 (0.04)	1.8 (0.07)	1.8 (0.07)	2.0 (0.08)
	Ambient	1.3 (0.05)	2.8 (0.11)	4.6 (0.18)	4.8 (0.19)	5.1 (0.20)
	422 (300)	3.8 (0.15)	7.1 (0.28)	7.6 (0.30)	8.1 (0.32)	8.9 (0.35)
	505 (450)	6.6 (0.26)	7.1 (0.28)	7.4 (0.29)	7.9 (0.31)	7.9 (0.31)
	533 (500)	8.1 (0.32)	8.1 (0.32)	8.6 (0.34)	9.1 (0.36)	22.1 (0.87)

Table 2.2.6 . Phase II Unstressed Thermal Aging—PPQ

## Individual Test Values—Lap Shear

## Initial Values

219K (-65°F)		Ambient		422K (300°F)		505K (450°F)		533K (500°F)	
MPa	psi	MPa	psi	MPa	psi	MPa	psi	MPa	psi
36.8	(5330)	29.3	(4260)	25.0	(3620)	18.3	(2660)	11.0	(1600)
30.1	(4360)	35.2	(5100)	26.1	(3780)	21.3	(3090)	13.9	(2020)
22.2	(3220)	29.1	(4220)	25.8	(3740)	17.8	(2580)	15.6	(2270)
32.8	(4760)	31.0	(4500)	21.7	(3150)	20.9	(3030)	12.7	(1840)
35.2	(5100)	33.2	(4820)	22.7	(3290)	22.6	(3280)	19.7	(2860)
36.6	(5310)	34.2	(4960)	29.6	(4300)	23.2	(3360)	17.0	(2460)
32.7	(4740)	33.2	(4820)	27.9	(4050)	20.7	(3000)	14.1	(2050)
35.3	(5130)	30.9	(4480)	24.7	(3580)	19.8	(2870)	16.4	(2380)
33.8	(4900)	35.4	(5140)	25.5	(3700)	21.8	(3160)	10.6	(1530)
36.1	(5240)	31.2	(4520)	23.4	(3380)	18.6	(2700)	20.8	(3020)
33.2	(4810)	32.3	(4680)	25.2	(3660)	20.5	(2970)	15.2	(2200)
									Average

## Lap Shear 100 Hours Aging at 505K (450°F)

219K (-65°F)		Ambient		422K (300°F)		505K (450°F)	
MPa	psi	MPa	psi	MPa	psi	MPa	psi
37.7	(5470)	34.9	(5060)	25.4	(3690)	20.0	(2900)
35.6	(5170)	30.3	(4400)	16.9	(2450)	24.1	(3490)
33.3	(4830)	33.6	(4870)	19.3	(2800)	20.4	(2960)
35.0	(5070)	34.3	(4980)	28.5	(4130)	21.2	(3070)
32.8	(4760)	28.7	(4160)	28.1	(4070)	18.0	(2610)
34.9	(5060)	32.3	(4690)	23.6	(3430)	20.8	(3010)
						Average	

## 500 Hours Aging at 505K (450°F)

MPa	psi	MPa	psi	MPa	psi	MPa	psi
34.9	(5060)	35.9	(5200)	28.6	(4140)	24.1	(3490)
32.1	(4660)	35.4	(5140)	24.2	(3510)	22.1	(3200)
36.4	(5280)	33.9	(4920)	21.2	(3080)	21.9	(3180)
33.7	(4890)	30.1	(4360)	27.4	(3970)	21.2	(3080)
28.5	(4130)	36.1	(5240)	25.7	(3730)	23.6	(3420)
33.1	(4800)	34.3	(4970)	25.4	(3690)	22.6	(3270)
						Average	

## 1000 Hours Aging at 505K (450°F)

MPa	psi	MPa	psi	MPa	psi	MPa	psi
27.9	(4050)	37.9	(5490)	30.3	(4400)	25.8	(3740)
30.3	(4390)	33.0	(4790)	24.1	(3500)	27.2	(3940)
33.9	(4910)	28.6	(4140)	25.1	(3640)	24.1	(3500)
26.5	(3840)	27.7	(4020)	27.0	(3920)	24.8	(3600)
32.8	(4760)	35.2	(5110)	27.6	(4000)	25.1	(3640)
30.3	(4390)	32.5	(4710)	26.8	(3890)	25.4	(3680)
						Average	

## 2000 Hours Aging at 505 (450°F)

MPa	psi	MPa	psi	MPa	psi	MPa	psi
31.0	(4500)	28.6	(4140)	29.0	(4200)	22.3	(3240)
32.7	(4740)	21.1	(3060)	21.2	(3080)	20.7	(3000)
18.5	(2680)	14.6	(2120)	21.4	(3100)	19.4	(2820)
23.4	(3400)	29.5	(4280)	20.0	(2900)	20.3	(2940)
27.7	(4020)	24.8	(3600)	24.8	(3600)	22.8	(3310)
26.7	(3870)	23.7	(3440)	23.3	(3380)	21.1	(3060)
						Average	

Table 2.2-7 Phase II Unstressed Thermal Aging—PPQ

## Individual Test Values—Peel

## Initial Values

219K (-65°F)		Ambient		422K (300°F)		505K (450°F)		533K (500°F)	
N·M	lb/in	N·M	lb/in	N·M	lb/in	N·M	lb/in	N·M	lb/in
0.56	(5.0)	0.56	(5.0)	0.77	(6.8)	1.22	(10.8)	1.02	(9.0)
0.58	(5.2)	0.58	(5.2)	0.86	(7.6)	0.45	(4.0)	0.31	(2.8)
0.81	(7.2)	0.61	(5.4)	0.79	(7.0)	0.90	(8.0)	0.93	(8.2)
0.61	(5.4)	0.63	(5.6)	0.86	(7.6)	1.04	(9.2)	0.97	(8.6)
0.77	(6.8)	0.58	(5.2)	0.68	(6.0)	0.97	(8.6)	1.31	(11.6)
0.67	(5.9)	0.60	(5.3)	0.79	(7.0)	0.91	(8.1)	0.90	(8.0)

## After 1000 Hours Aging at 505K (450°F)

N·M	lb/in	N·M	lb/in	N·M	lb/in	N·M	lb/in
0.58	(5.2)	0.58	(5.2)	0.74	(6.6)	0.81	(7.2)
0.58	(5.2)	0.63	(5.6)	0.74	(6.6)	0.70	(6.2)
0.58	(5.2)	0.58	(5.2)	0.70	(6.2)	0.68	(6.0)
0.56	(5.0)	0.54	(4.8)	0.56	(5.0)	0.77	(6.8)
0.74	(6.6)	0.74	(6.6)	0.70	(6.2)	0.77	(6.8)
0.61	(5.4)	0.62	(5.5)	0.69	(6.1)	0.74	(6.6)

## After 500 Hours Aging at 505K (450°F)

N·M	lb/in	N·M	lb/in	N·M	lb/in	N·M	lb/in
0.56	(5.0)	0.79	(7.0)	0.61	(5.4)	0.70	(6.2)
0.66	(5.8)	0.66	(5.8)	0.61	(5.4)	0.88	(7.8)
0.70	(6.2)	0.56	(5.0)	0.61	(5.4)	0.88	(7.8)
0.63	(5.6)	0.56	(5.0)	0.61	(5.4)	0.56	(5.0)
0.54	(4.8)	0.63	(5.6)	0.61	(5.4)	0.72	(6.4)
0.62	(5.5)	0.64	(5.7)	0.61	(5.4)	0.74	(6.6)

## After 1000 Hours Aging at 505K (450°F)

N·M	lb/in	N·M	lb/in	N·M	lb/in	N·M	lb/in
0.63	(5.6)	0.68	(6.0)	0.77	(6.8)	0.61	(5.4)
0.77	(6.8)	0.66	(5.8)	0.77	(6.8)	0.99	(8.8)
0.63	(5.6)	0.66	(5.8)	0.77	(6.8)	0.68	(6.0)
0.84	(7.4)	0.61	(5.4)	0.68	(6.0)	0.75	(6.6)
0.54	(4.8)	0.70	(6.2)	0.77	(6.8)	0.81	(7.2)
0.68	(6.0)	0.66	(5.8)	0.75	(6.6)	0.77	(6.8)

## After 2000 Hours Aging at 505K (450°F)

N·M	lb/in	N·M	lb/in	N·M	lb/in	N·M	lb/in
0.54	(4.8)	0.43	(3.8)	0.41	(3.6)	0.56	(5.0)
0.56	(5.0)	0.50	(4.4)	0.41	(3.6)	0.90	(8.0)
0.50	(4.4)	0.45	(4.0)	0.34	(3.0)	0.56	(5.0)
0.36	(3.2)	0.66	(5.8)	0.54	(4.8)	0.81	(7.2)
0.45	(4.0)	0.50	(4.4)	0.54	(4.8)	0.95	(8.4)
0.48	(4.3)	0.51	(4.5)	0.45	(4.0)	0.76	(6.7)

Table 2.2-8. Phase II Unstressed Thermal Aging—PPQ

## Individual Test Values—Crack Extension

	Initial Crack Length		Exposure Temperature	1 Hour Exposure		100 Hour Exposure		500 Hour Exposure		
	mm	inch		mm	inch	mm	inch	mm	inch	
	23.4	(0.92)	219K (-65°F)	1.0	(0.04)	1.0	(0.04)	1.8	(0.07)	
	23.1	(0.97)		"	1.3	(0.05)	1.3	(0.05)	1.3	(0.05)
	24.9	(0.98)		"	1.0	(0.04)	1.8	(0.07)	2.7	(0.11)
	28.4	(1.12)		"	0.0	(0.0)	0.0	(0.0)	0.8	(0.03)
	23.1	(0.91)		"	1.5	(0.06)	1.5	(0.06)	2.5	(0.10)
Avg.	24.6	(0.97)	"	1.0	(0.04)	1.0	(0.04)	1.8	(0.07)	
	26.7	(1.05)	Ambient	1.8	(0.07)	4.3	(0.17)	5.8	(0.23)	
	25.9	(1.02)		"	0.0	(0.0)	1.0	(0.04)	2.0	(0.08)
	23.4	(0.92)		"	1.3	(0.05)	2.0	(0.08)	3.0	(0.12)
	24.6	(0.97)		"	3.5	(0.14)	4.6	(0.18)	7.1	(0.28)
	24.4	(0.96)		"	0.0	(0.0)	2.0	(0.08)	4.8	(0.19)
Avg.	24.9	(0.98)	"	1.3	(0.05)	2.8	(0.11)	4.6	(0.18)	
	24.1	(0.95)	422K (300°F)	4.8	(0.19)	9.9	(0.39)	10.7	(0.42)	
	23.4	(0.92)		"	3.6	(0.14)	7.6	(0.30)	7.6	(0.30)
	25.4	(1.00)		"	4.6	(0.18)	10.7	(0.42)	12.2	(0.48)
	23.6	(0.93)		"	3.3	(0.13)	3.3	(0.13)	4.3	(0.17)
	22.6	(0.89)		"	2.8	(0.11)	3.8	(0.15)	3.8	(0.15)
Avg.	23.9	(0.94)	"	3.8	(0.15)	7.1	(0.28)	7.6	(0.30)	
	23.1	(0.91)	505K (450°F)	3.3	(0.13)	4.6	(0.18)	4.6	(0.18)	
	23.9	(0.94)		"	17.0	(0.67)	17.0	(0.67)	18.3	(0.72)
	24.6	(0.97)		"	2.3	(0.09)	2.3	(0.09)	2.3	(0.09)
	23.1	(0.91)		"	4.1	(0.16)	5.3	(0.21)	5.3	(0.21)
	23.6	(0.93)		"	5.8	(0.23)	5.8	(0.23)	5.8	(0.23)
Avg.	23.6	(0.93)	"	6.6	(0.26)	7.1	(0.28)	7.4	(0.29)	
	25.6	(1.01)	533K (500°F)	7.4	(0.29)	7.4	(0.29)	7.4	(0.29)	
	24.4	(0.96)		"	6.8	(0.27)	6.8	(0.27)	6.8	(0.27)
	25.4	(1.00)		"	6.6	(0.26)	6.6	(0.26)	6.6	(0.26)
	23.6	(0.93)		"	7.6	(0.30)	7.6	(0.30)	8.4	(0.33)
	24.1	(0.95)		"	12.4	(0.49)	12.4	(0.49)	13.5	(0.53)
Avg.	24.6	(0.97)	"	8.1	(0.32)	8.1	(0.32)	8.6	(0.34)	

Lap-shear specimens are being loaded to 25 and 50% of ultimate stress at -65, +70, and removed and tested for residual strength at the exposed temperature. The time intervals indicated may vary depending upon the results of the stress-rupture data from Task I and as data are accumulated from these tests. Three lap-shear specimens are being tested for each data point. Data are presented for the 0, 100, 1,000 and 2,000-hour intervals in Tables 2.2-9 and 2.2.10.

#### Humidity Exposure

Lap-shear, T-peel, and crack-extension specimens have been exposed for 2,000 hours in a humidity cabinet under conditions of 120°9F and 95% RH. Specimens were removed and immediately tested at -65, ambient, and +450°9F for exposure conditions of 1,000 and 2,000 hours (five specimens per data point). Lap-shear strength, T-peel strength, and crack-extension length were recorded, as well as the mode of failure. A summary of the data is presented in Table 2.2-11. Individual test values are listed in Table 2.2-12.

#### Aircraft Fluid Exposure

The resistance of the adhesives to common aircraft fluids was assessed. Lap-shear and crack-extension specimens were submerged in selected fluids as follows:

1. JP-4 jet fuel, ambient
2. MIL-H-5606 hydraulic fluid, ambient and 344K (160°9F)
3. Skydrol hydraulic fluid, ambient and 344K (160°9F)
4. MIL-H-7808 lubricant, ambient
5. Deicing fluid, ambient

PPQ specimens were tested after 30 and 60 days exposure at ambient temperature for all fluids. In addition, tests were conducted after 30 and 60 days 344K (160°9F) exposure to MIL-H-5056 and Skydrol exposure and test at ambient for all fluids for up to 5,000 hours will be conducted.

## APPENDIX

Table 2.2-10. Phase II Stressed Thermal Aging--PPQ

Individual Test Values--Lap Shear

PERCENT OF Ultimate	Stress Load		Temperature		Exposure Time					
					Initial		100 Hours		1000 Hours	
	MPa	psi	K	(°F)	MPa	psi	MPa	psi	MPa	psi
25	8.28	(1200)	219	(-65)	29.4	(4270)	36.2	(5250)	36.8	(5340)
25	"	"	"	"	27.8	(4030)	33.0	(4790)	39.3	(5700)
25	"	"	"	"	32.1	(4650)	35.4	(5130)	36.8	(5340)
					29.8	(4320)	34.9	(5060)	37.7	(5460)
50	10.3	(1500)	"	"	31.5	(4570)	33.6	(4870)	38.3	(5560)
50	"	"	"	"	30.8	(4460)	34.6	(5020)	34.6	(5020)
50	"	"	"	"	29.5	(4280)	33.9	(4910)	36.4	(5280)
					30.6	(4440)	34.0	(4930)	36.5	(5290)
25	8.28	(1200)	Ambient	"	26.1	(3790)	35.0	(5070)	32.1	(4660)
25	"	"	"	"	33.9	(4920)	35.3	(5120)	27.6	(4000)
25	"	"	"	"	33.4	(4840)	30.8	(4470)	34.2	(4960)
					31.2	(4520)	33.7	(4890)	31.3	(4540)
50	10.3	(1500)	"	"	31.6	(4580)	33.2	(4810)	36.0	(5220)
50	"	"	"	"	34.1	(4940)	35.1	(5090)	32.0	(4640)
50	"	"	"	"	34.9	(5060)	35.4	(5140)	35.6	(5160)
					33.5	(4860)	34.6	(5010)	34.6	(5010)
25	5.1	(740)	505	(450)	21.4	(3100)	21.0	(3050)	23.2	(3370)
25	"	"	"	"	19.9	(2880)	18.8	(2730)	17.7	(2560)
25	"	"	"	"	19.9	(2890)	24.1	(3490)	18.6	(2690)
					20.4	(2960)	21.3	(3090)	19.8	(2870)
50	10.2	(1480)	"	"	20.7	(3000)	24.2	(3510)	19.7	(2860)
50	"	"	"	"	21.6	(3130)	24.3	(3520)	23.0	(3340)
50	"	"	"	"	16.6	(2400)	17.5	(2540)	21.2	(3070)
					19.6	(2840)	22.0	(3190)	21.3	(3090)

Table 2.2-11. Humidity Exposure--PPQ

## Data Summary

Test Coupon	Test Temperature K (°F)	Exposure Time		Failure Mode Percent Cohesive)	
		1000 hours	2000 hours	1000 hours	2000 hours
Lap Shear, MPa (psi)	219 (-65)	27.9 (4040)	26.8 (3890)	90-100	80-90
	Ambient	25.8 (3740)	20.6 (2980)	60-70	60-70
	505 (450)	14.8 (2150)	12.1 (1760)	85-90	70-80
T-Peel, N·M (lb/in.)	219 (-65)	0.50 (4.4)	0.47 (4.2)	80-90	
	Ambient	0.52 (4.6)	0.38 (3.4)	40-60	
	505 (450)	0.77 (6.8)	0.81 (7.2)	10-20	
Crack Extension, mm (inch)		<u>Exposure Time</u>		<u>Extension</u>	
Initial crack, 24.4 (0.96)		1 hour		4.8 (0.19)	
		24 hours		14.5 (0.57)	
		100 hours		18.8 (0.74)	
		500 hours		20.1 (0.79)	
		1000 hours		21.3 (0.84)	
		2000 hours		22.1 (0.87)	

Table 2.2-12. Phase II Humidity Exposure (120°F/95% RH)  
Individual Test Values--PPQ

Test	Test Temperature K (°F)	Exposure Time, Hours		Failure Mode (Percent Cohesive)	
		1000	2000		
Lap Shear, MPa (psi)	219 (-65)	29.6 (4300)	24.1 (3500)		
	"	26.1 (3790)	24.1 (3500)		
	"	26.8 (3890)	30.8 (4460)		
	"	28.1 (4080)	32.1 (4660)		
	"	27.9 (4050)	23.0 (3340)		
Average	"	27.9 (4040)	26.8 (3890)	90-100	80-90
	Ambient	27.1 (3930)	15.7 (2280)		
	"	22.7 (3290)	22.1 (3200)		
	"	25.6 (3720)	19.4 (2810)		
	"	21.5 (3120)	23.9 (3460)		
	"	31.9 (4620)	21.6 (3140)		
Average	"	25.8 (3740)	20.6 (2980)	60-70	60-70
	505 (450)	9.8 (1420)	9.8 (1420)		
	"	18.3 (2650)	14.1 (2050)		
	"	11.9 (1720)	13.4 (1940)		
	"	18.9 (2740)	8.8 (1270)		
	"	15.2 (2200)	14.5 (2100)		
Average	"	14.8 (2150)	12.1 (1760)	85-90	70-80
Peel, N·M (lb/in)	219 (-65)	0.50 (4.4)	0.47 (4.2)	80	95
	"	0.50 (4.4)	0.45 (4.0)	80	70
	"	0.50 (4.4)	0.54 (4.8)	90	95
	"	0.52 (4.6)	0.43 (3.8)	85	95
	"	0.47 (4.2)	--	70	--
Average	"	0.50 (4.4)	0.47 (4.2)		
	Ambient	0.52 (4.6)	0.45 (4.0)	70	40
	"	0.52 (4.6)	0.38 (3.4)	40	40
	"	0.54 (4.8)	0.50 (4.4)	50	0
	"	0.47 (4.2)	0.20 (1.8)	50	--
Average	"	0.52 (4.6)	0.38 (3.4)		
	505 (450)	0.79 (7.0)	1.02 (9.0)	5	50
	"	0.86 (7.6)	0.81 (7.2)	5	50
	"	0.68 (6.0)	0.79 (7.0)	10	0
	"	0.74 (6.6)	0.61 (5.4)	10	0
Average	"	0.77 (6.8)	0.81 (7.2)		

Crack Extension mm(inch)

Initial Value, mm (inch)	1 Hour	24 Hours	100 Hours	500 Hours	1000 Hours	2000 Hours
25.9 (1.02)	3.8 (0.15)	13.7 (0.54)	17.0 (0.67)	19.8 (0.78)	22.1 (0.87)	22.9 (0.90)
23.6 (0.93)	6.9 (0.27)	17.0 (0.67)	19.8 (0.78)	20.8 (0.82)	22.4 (0.88)	22.4 (0.88)
24.1 (0.95)	3.0 (0.12)	12.4 (0.49)	18.0 (0.71)	24.9 (0.98)	24.9 (0.98)	25.6 (1.01)
23.6 (0.93)	3.3 (0.13)	14.5 (0.57)	19.6 (0.77)	20.8 (0.82)	22.6 (0.89)	23.4 (0.92)
24.1 (0.95)	7.1 (0.28)	15.0 (0.59)	20.1 (0.79)	14.5 (0.57)	14.5 (0.57)	15.7 (0.62)
24.4 (0.96)	4.8 (0.19)	14.5 (0.57)	18.8 (0.74)	20.1 (0.79)	21.3 (0.84)	22.1 (0.87)

The data generated thus far are too preliminary to make any general conclusions except for the effect of Skydrol at both ambient and 344K (160°F) on PPQ adhesive properties. As seen in Table 2.3.2-8, the initial lap-shear strength at 344K (160°F) in Skydrol drops from about 34.5 MPa (5,000 psi) to about 26.2 MPa (3,800 psi). Crack extensions of 18.5 mm (0.73 inch) (ambient) and 31.8 mm (1.25 inches) 344K (160°F) are significantly greater than for the other fluids.

The summary of test values for fluid exposure is contained in Table 2.2-13. Individual test values are found in Table 2.2-14 and Table 2.2-15.

Samples were exposed for 30 and 60 days and tested at ambient temperatures for residual strength. Three specimens were tested per determination. Specimens are also being exposed to the above fluids at 70°F for 5,00 hours.

#### Extended Exposure

To permit NASA to obtain 50,000-hour aging data on lap-shear specimens, Boeing will fabricate 100 extra lap-shear specimens and 12 crack-propagation specimens at the same time that the stressed and unstressed thermal aging specimens are fabricated. Specimens will be inserted into the aging chamber at 450°F in an unstressed condition and in a stressed (50% of ultimate) condition at the same time that the initial aging specimens are started. If NASA elects to extend the contract and continue the aging program after the 36-month contract period, the specimens will be removed and tested at appropriate time intervals (e.g., 10,000; 20,000; 30,000; 40,000; and 50,000 hours). If the contract is not extended, all specimens will be delivered to the NASA project monitor.

#### Thermal Cycling

Lap-shear, T-peel, and crack-extension specimens will be thermally cycled from -65 to +450°F at the rate of 30 minutes per cycle. Specimens will be tested after 1,000 and 2,000 thermal cycles. Five lap-shear and five T-peel specimens will be tested for residual strength at 70 and 450°F; the crack-extension specimens will be examined and measured for crack propagation at each time interval.

Table 2.2-13. Aircraft Fluid Exposure, PPQ

Test Coupon	Duration	MIL-H-5606			Skydrol		MIL-H-7308 Ambient	Deicing Fluid Ambient
		JP-4 Ambient	Ambient	344K (160°F)	Ambient	344K (160°F)		
Lap Shear, MPa	30 days	33.0 (4780)	32.1 (4660)	35.3 (5120)	34.7 (5030)	26.3 (3810)	27.7 (4020)	33.3 (4830)
	60 days	32.8 (4750)	30.8 (4470)	35.0 (5080)	30.6 (4430)	26.3 (3810)	33.0 (4780)	34.7 (5030)
Crack Extension, mm (inches) growth	30 days	3.3 (0.13)	3.3 (0.13)	5.6 (0.22)	18.5 (0.73)	31.8 (1.25)	13.2 (0.52)	3.8 (0.15)
	60 days	3.3 (0.13)	9.1 (0.36)	6.8 (0.27)	19.6 (0.77)	33.8 (1.29)	13.2 (0.52)	3.8 (0.15)

Table 2.2-14. Phase II Fluid Exposure  
Lap Shear Individual Test Values, MPa (psi)

Exposure Fluid	Exposure Temperature			
	Ambient		344K (160°F)	
	Exposure Time		Exposure Time	
	30 Days	60 Days	30 Days	60 Days
JP-4	31.0 (4500)	32.6 (4730)	--	--
	35.1 (5090)	34.6 (5010)	--	--
	32.2 (4760)	31.2 (4520)	--	--
	33.0 (4780)	32.8 (4750)	--	--
MIL-H-5056	34.5 (4710)	31.7 (4590)	32.1 (4650)	34.6 (5020)
	35.9 (5210)	31.6 (4580)	36.8 (5340)	32.9 (4770)
	27.9 (4050)	29.3 (4250)	37.0 (5360)	37.6 (5450)
	32.1 (4660)	30.8 (4470)	35.3 (5120)	35.0 (5080)
Skydrol	32.8 (4750)	31.0 (4490)	26.1 (3780)	25.6 (3710)
	37.6 (5460)	31.2 (4520)	24.6 (3560)	24.7 (3580)
	33.7 (4890)	29.6 (4290)	28.2 (4090)	28.5 (4130)
	34.7 (5030)	30.6 (4430)	26.3 (3810)	26.3 (3810)
MIL-H-7808	31.8 (4610)	29.9 (4340)	--	--
	31.2 (4530)	36.1 (5230)	--	--
	20.2 (2930)	32.9 (4770)	--	--
	27.7 (4020)	33.0 (4780)	--	--
Deicing Fluid	33.2 (4810)	31.6 (4580)	--	--
	28.8 (4170)	35.3 (5120)	--	--
	38.0 (5510)	37.2 (5390)	--	--
	33.3 (4830)	34.7 (5030)	--	--

Table 2.2-15. Phase II Fluid Exposure  
Crack Extension Individual Test Values, mm (inches)

Exposure Fluid	Exposure Temperature					
	Ambient			344K (160°F)		
	Exposure Time			Exposure Time		
	Initial	30 Days	60 Days	Initial	30 Days	60 Days
JP-4	23.4 (0.92)	3.0 (0.12)	3.0 (0.12)	--	--	--
	25.4 (1.00)	3.0 (0.12)	3.0 (0.12)	--	--	--
	24.6 (0.97)	3.6 (0.14)	3.6 (0.14)	--	--	--
		3.3 (0.13)	3.3 (0.13)	--	--	--
MIL-H-5056	24.4 (0.96)	2.3 (0.09)	4.6 (0.18)	31.0 (1.22)	2.5 (0.10)	4.6 (0.18)
	25.9 (1.02)	10.7 (0.42)	12.2 (0.48)	23.6 (0.93)	4.8 (0.19)	4.8 (0.19)
	24.9 (0.98)	10.9 (0.43)	10.9 (0.43)	28.2 (1.11)	9.1 (0.36)	11.4 (0.45)
		7.9 (0.31)	9.1 (0.36)		5.6 (0.22)	6.9 (0.27)
Skydrol	25.6 (1.01)	17.5 (0.69)	18.8 (0.74)	24.9 (0.98)	38.6 (1.52)	40.6 (1.60)
	23.6 (0.93)	15.0 (0.59)	16.5 (0.65)	25.6 (1.01)	24.4 (0.96)	24.4 (0.96)
	26.2 (1.03)	23.4 (0.92)	23.4 (0.92)	25.1 (0.99)	32.0 (1.26)	33.3 (1.31)
		18.5 (0.73)	19.6 (0.77)		31.8 (1.25)	32.8 (1.29)
MIL-H-7808	27.9 (1.10)	17.3 (0.68)	17.3 (0.68)	--	--	--
	23.6 (0.93)	10.7 (0.42)	10.7 (0.42)	--	--	--
	24.9 (0.98)	11.9 (0.47)	11.9 (0.47)	--	--	--
		13.2 (0.52)	13.2 (0.52)	--	--	--
Deicing Fluid	24.6 (0.97)	3.6 (0.14)	3.6 (0.14)	--	--	--
	24.4 (0.96)	3.6 (0.14)	3.6 (0.14)	--	--	--
	29.0 (1.14)	4.6 (0.18)	4.6 (0.18)	--	--	--
		3.8 (0.15)	3.8 (0.15)	--	--	--

## 2.4 PHASE II—MATERIAL AND PROCESS SPECIFICATIONS

The materials and process specification for high temperature adhesives prepared in rough draft form are attached as an appendix to this report. They have been patterned after specification formats utilized by Boeing.

### 3.0 PROGRAM STATUS

#### 3.1 PHASE I—ADHESIVE SCREENING

- o Ten candidate adhesive systems were selected as specified in the contract statement of work section 3.1.A.
- o Eight different Ti-6Al-4V surface treatments have been investigated for each of the 10 adhesive resins per statement of work section 3.1.B.
- o Primers (two for each adhesive resin) have been investigated for appropriate cures and thickness per statement of work section 3.1.C.
- o Initial evaluation of bonded joints using various combinations of the above adhesive resins and surface treatments has been completed per statement of work section 3.1.D.
- o Selection of four adhesive systems (primer, adhesive resin, and surface treatments) per statement of work section 3.1.E was attempted. However, based upon the data generated during initial evaluation, the three systems selected represent the major types of adhesive systems (i.e., PPQ, condensation polyimide, and additional polyimides presently available. Evaluation of these candidates should yield data that are representative of their types of polymers). This decision was reached with the concurrence and approval of the NASA Technical Representative of the Contracting Officer.
- o One lap-shear adherend surface-treated and primed by each process was shipped to Dr. Jim Wightman of Virginia Polytechnic Institute per statement of work section 3.B.
- o Cure cycle optimization studies for each adhesive system per statement of work section 3.1.E(1) have been completed.
- o Properties versus temperature have been completed on each adhesive system per statement of work section 3.1.E(2), except for T-peel coupons, which were removed from the test matrix. T-peel was replaced with hand peel for each system at room temperature with concurrence of the NASA Technical Monitor.
- o Thermal aging characteristics per statement of work section 3.1.E(3) have been initiated. Aging has been completed through 10,000 hours.
- o Humidity aging characteristics per statement of work section 3.1.E(4) have been initiated. Aging has been completed through 5,000 hours.
- o Large-area bonding per statement of work section 3.1.F has been completed.

- o Surface characterization and failure analysis per statement of work section 3.1.G have been largely completed.
- o Fractured lap-shear specimens per Part IX, Delivery, Item Description No. 1 have been shipped to Virginia Polytechnic Institute and State University.
- o Fractured lap-shear specimens per statement of work section 3.1.B have been delivered for surface characterization and failure analysis per statement of work section 3.1.G.
- o NR056X and PPQ were selected for continued evaluation in Phase II.
- o LARC-2 (LARC-TPI) was added to Phase II evaluation.

### 3.2 PHASE II—ADHESIVE OPTIMIZATION AND CHARACTERIZATION

- o Phase II Task I, per statement of work section 3.2, has been initiated.
- o Adhesive resin batches of PPQ and NR056X have been received and chemical analysis completed per statement of work section 3.2.A.
- o Titanium sheet required for test coupons in Phase II has been received.
- o Optimization of formulation, process, and surface treatment is in progress for PPQ, LARC-2, and NR056X.
- o Rough draft material and process specifications have been prepared for PPQ and LARC-2.
- o Cure cycle thermal aging data, 505K (450°F) to 3,000 hours, have been completed.
- o NR056X is being dropped from the program.
- o Phase II Task II per statement of work Section 3.2.B has been initiated for PPQ.
- o Stressed thermal aging to 1,000 hours has been completed for PPQ.
- o Unstressed thermal aging to 1,000 hours has been completed for PPQ.
- o Humidity aging to 2,000 hours has been completed for PPQ.
- o Aircraft fluids exposure to 6 days has been completed for PPQ.
- o Extended exposure has been initiated for PPQ.

#### 4.0 WORK PLANNED FOR THE NEXT 6 MONTHS

During the next 6 months, program activity will include:

- o Continuation of Phase I thermal aging tests
- o Continuation of Phase II aging for PPQ
- o Initiation of Phase II evaluation and aging for LARC-TPI
- o Resolution of titanium surface oxide failure analysis

## MATERIAL SPECIFICATION

### HIGH TEMPERATURE STABLE (450°F) STRUCTURAL ADHESIVES FOR BONDED TITANIUM ASSEMBLIES

#### 1.0 SCOPE

- a. This document establishes the requirements and tests for supplier qualification and purchaser inspection of adhesive suitable for structural bonding sandwich and metal-to-metal assemblies suitable for continuous service at elevated temperatures when bonded in accordance with.....
- b. This specification requires qualified products.

#### 2.0 CLASSIFICATION

##### 2.1 Class

The adhesive systems shall consist of two classes.

Class 1 Polyphenyquinoxaline (PPQ) Resin and Solvent

Class 2 LARC-13 Resin with aluminum filler and solvent

##### 2.2 Types

Type 1 - will consist of the liquid adhesive with solvent.

Type 2 - will consist of an adhesive film supported with 112 E-glass/ A1100 finish.

Type 3 - will consist of an unsupported film of the adhesive.

##### 2.3 Grades (Type 2 Only)

Grade A -  $0.060 \pm .010$  lbs/ft<sup>2</sup> adhesive film with separator sheet(s).

Grade B -  $0.080 \pm 0.10$  lbs/ft<sup>2</sup> adhesive film with separator sheet(s).

Grade C -

#### 3.0 REFERENCES

#### 4.0 DEFINITIONS

Batch - A batch shall consist of a homogeneous unit of finished adhesive manufactured under controlled conditions at one time or representing a blend of several manufactured units of finished adhesive of the same formulation.

Lot - A lot shall consist of all of the adhesive from one adhesive batch received in one shipment.

Lot Size - Lot size refers to the total number of units in any one lot irrespective of the volume of the container or length of the roll.

Unit - A unit refers to the smallest single portion of adhesive received in any one LOT, i.e., a roll of tape adhesive or a container of liquid adhesive.

## 5.0 MATERIAL REQUIREMENTS

### 5.1 Physical Properties

#### 5.1.1 Quality Type 1 & 2

Material when visually examined shall be free from foreign materials.

#### 5.1.2 Consistency Type 1 Adhesive

Type 1 when agitated must readily form homogenous mixture.

#### 5.1.3 Storage Life

Type 1 and 2 adhesive must meet physical requirements after 180 days from date of manufacture when packaged according to Section .

#### 5.1.4 Adhesive Weight Type 2 Only

Determine adhesive weight of Class I and II, Type 2, Grades A, B and C according to Section 8.8.

#### 5.1.5 Percent Volatile Type 2 Only

Determine percent volatile of Class I and II, Type 2, Grades A, B and C according to Section .

#### 5.1.6 Percent Solid of Type 1

Percent solid of Class I and II, Type 1 shall be the following when tested according to Section 8.9.

Class I	Type 1	$9 \pm 1\%$
Class II	Type 2	$26 \pm 2\%$

## 6.0 QUALIFICATION

- a. Direct all requests for qualification to the Material Department which will request data and samples when desired for qualification purposes.
- b. Test data supplied must give test values obtained and not use the word "conforms" showing the adhesive meets requirements of Section 5 and Tables I and II. The required number of standard test specimens for each test specified in Table III shall be fabricated and tested per Section 8. The data shall state the test facility (supplier or named test laboratory) used in determination of the data.
- c. After review of supplier data, the supplier will be advised as to whether adhesive approval has been granted.
- d. No changes in raw materials or processing shall be made without notification and prior approval in writing. Any change may require requalification.

TABLE I

## PHYSICAL PROPERTIES OF METAL TO METAL SPECIMENS

TEST	TEST REFERENCE SECTIONS				NUMBER OF SPECIMENS PER BATCH	TOTAL	MINIMUM REQUIREMENTS	
							AVERAGE	INDIVIDUAL
1. Lap Shear at $75 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.2.3.a	8.2.3.b	10	30		
2. Lap Shear at $-65 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.2.3.a	8.2.3.c	10	30		
3. Lap Shear at $450 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.2.3.a	8.2.3.d	10	30		
4. Lap Shear at $75 \pm 5^\circ\text{F}$ After 500 Hours at $450 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.2.3.a	8.2.3.b	5	15		
5. Lap Shear at $450 \pm 5^\circ\text{F}$ After 500 Hours at $450 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.2.3.a	8.2.3.d	5	15		
6. Lap Shear at $75 \pm 5^\circ\text{F}$ After 1000 Hours at $450 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.2.3.a	8.2.3.b	5	15		
7. Lap Shear at $450 \pm 5^\circ\text{F}$ After 1000 Hours at $450 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.2.3.a	8.2.3.d	5	15		
8. Lap Shear at $75 \pm 5^\circ\text{F}$ After 5000 Hours at $450 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.2.3.a	8.2.3.b	5	15		
9. Lap Shear at $450 \pm 5^\circ\text{F}$ After 5000 Hours at $450 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.2.3.a	8.2.3.d	5	15		
10. Fatigue Strength at $75 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.3.1		5	15	N/A	$10^6$ Cycles/Min at 1200 PSI Max
11. Fatigue Strength at $450 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.3.2		5	15	N/A	$10^6$ Cycles/Min at 750 PSI Max
12. Creep-Rupture-Deformation at $75 \pm 5^\circ\text{F}$ Under 1600 PSI for 500 Hours	8.2.1	8.2.2	8.3.2		4	12	N/A	0.015 Inches Max Deformation

TABLE I (Con't)

	TEST	TEST REFERENCE SECTIONS				NUMBER OF SPECIMENS		MINIMUM REQUIREMENTS	
						PER BATCH	TOTAL	AVERAGE	INDIVIDUAL
	13. Creep-Rupture-Deformation at $450 \pm 5^\circ\text{F}$ Under 800 PSI for 500 Hours	8.2.1	8.2.2	8.4.2		4	12	N/A	.015 Inches Max Deformation
	14. Shear at $75 \pm 5^\circ\text{F}$ After 30 Days Salt Spray Exposure at $95 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.2.3.a	8.2.3.e	5	15		
	15. Lap Shear at $75 \pm 5^\circ\text{F}$ After Exposure to 95-100% Relative Humidity at $120 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.2.3.a	8.2.3.f	5	15		
75	16. Lap Shear at $75 \pm 5^\circ\text{F}$ After 30 Days Immersion in Jet Fuel Grade 2 MIL-J-5161 at $75 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.2.3.a	8.2.3.g	5	15		
	17. Lap Shear at $75 \pm 5^\circ\text{F}$ After 30 Days Immersion In MIL-H-5606 at $75 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.2.3.a	8.2.3.h	5	15		
	18. Lap Shear at $75 \pm 5^\circ\text{F}$ After Immersion in MIL-H-7807 at $75 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.2.3.a	8.2.3.i	5	15		
	19. Lap Shear at $75 \pm 5^\circ\text{F}$ After Immersion in Aircraft De-Ice Fluid at $75 \pm 5^\circ\text{F}$	8.2.1	8.2.2	8.2.3.a	8.2.3.j	5	15		
	20. T-Peel at $75 \pm 5^\circ\text{F}$	8.5.1	8.5.2	8.5.4		5	15		
	21. T-Peel at $450 \pm 5^\circ\text{F}$	8.5.1	8.5.2	8.5.4		5	15		
	22. T-Peel at $75 \pm 5^\circ\text{F}$ After 1000 Hours at $450 \pm 5^\circ\text{F}$	8.5.1	8.5.2	8.5.3		5	15		
	23. T-Peel at $450 \pm 5^\circ\text{F}$ After 1000 Hours at $450 \pm 5^\circ\text{F}$	8.5.1	8.5.2	8.5.4		5	15		

TABLE II  
PHYSICAL PROPERTIES OF HONEYCOMB SPECIMENS

TESTS	REFERENCES	NO. OF SPECIMENS PER BATCH	REQUIRED TOTAL	MINIMUM REQUIREMENTS	
				AVERAGE	INDIVIDUAL
1. Flatwise Tensile at 75 ± 5°F	8.7.1	5	15		
2. Flatwise Tensile at -65 ± 5°F	8.7.1	5	15		
3. Flatwise Tensile at 450 ± 5°F	8.7.1	5	15		
4. Flatwise Tensile at 75 ± 5°F After 1000 Hours at 450 ± 5°F	8.7.1	5	15		
5. Flatwise Tensile at 450 ± 5°F	8.7.1	5	15		
6. Honeycomb Peel at 75 ± 5°F	8.7.2	5	15		
7. Honeycomb Peel at 450 ± 5°F	8.7.2	5	15		

TABLE III  
ENVIRONMENTAL DURABILITY TEST

1. Crack Extension After 1000 Hours at 95 ± 5°F	8.6.1	8.6.2	5	15		
2. Crack Extension After 1000 Hours at 450 ± 5°F	8.6.1	8.6.2	5	15		
3. Crack Extension After 1000 Hours at 95-100% Relative Humidity and 120°F	8.6.1	8.6.2	5	15		
4. Lab Shear Sustained Stress Loading at 95-100% Relative Humidity and 120°F	8.6.3		4	12	N/A	No Failure in 1000 Hour Aging

## 7.0 QUALITY CONTROL

### 7.1 General

All materials covered by this specification shall be subjected to both supplier and purchaser inspection to determine compliance with the requirements of this specification.

### 7.2 Supplier Inspection

- a. The supplier shall verify that each production shipment has been manufactured from identical materials and by identical methods to those approved for the qualification samples.
- b. Supplier shall test each production shipment in accordance with the requirements of Section 6.4 and each shipment shall be accompanied by a test report providing the results of such testing.
- c. All areas of Type II film adhesive which are not suitable for structural adhesive bonding shall be legibly marked by the supplier and deducted from the roll yardage.

### 7.3 Purchaser Inspection

- a. Each roll or container of adhesive shall be checked for compliance with the identification requirements of Section 8. All packages incorrectly identified shall not be released for storage or production until the correct information has been marked on the package, as required by Section 8.
- b. LOT NUMBERS shall be established at the time of receipt and marked on each unit of adhesive received in the lot.
- c. The acceptance tests of Table IV are mandatory on each sample of each lot of adhesive.
- d. In addition to the tests specifically listed as acceptance tests, any other test described in Section 4 of this specification may be used to assure that production shipments of adhesive conform to the requirements of this specification and are comparable to the material previously qualified.

### 7.4 Sampling, Acceptance, and Rejection Criteria

- a. The sampling unit shall be as follows:
  - (1) Type I Adhesive - Container (Normally 5 gallon capacity)
  - (2) Type II Film Adhesive - Roll
- b. One sample per unit is required for acceptance inspection testing. Each sample shall be taken from different units.
- c. Each unit sample shall be of an amount sufficient to conduct all required tests.
- d. The number of units of adhesive (sample size) to be tested from each lot under the double variables sampling plan is dependent upon the size of the lot. The sample size shall be as given in Table V. For weight test, randomly select two rolls only from the sample units selected in Table V.
- e. Compute the Quality Index ( $Q_L$ ) in accordance with the following equations:

$$\bar{X} = \frac{\sum X}{n}$$

$$S = \frac{n \sum X^2 - (\sum X)^2}{n(n-1)}$$

$$Q_L = \frac{\bar{X} - L}{S}$$

#### 7.4 (Continued)

Where:

$X$  = Individual test value for each specimen

$\bar{X}$  = Average value for each test

$S$  = Standard deviation for individual specimens

$n$  = Number of individual specimens tested in accordance with Tables IV and V

$L$  = Minimum Requirement (L Value) per Tables I and II

- f. The lot of adhesive undergoing Acceptance testing shall have the testing continued or shall be accepted or rejected as specified below:
- (1) ACCEPT THE LOT when the computed Quality Index for the first sample equals or exceeds the Quality Index Requirement (k) of Column A, Table V for the size of lot undergoing Acceptance testing.
  - (2) REJECT THE LOT when the computed Quality Index for the first sample equals or is less than the Quality Requirement of Column B, Table V for the size of lot undergoing Acceptance testing or when any individual value is less than the L value of Tables I and II.
  - (3) CONTINUE TESTING with a second sample from the lot when the computed Quality Index for the first sample falls between the Quality Index Requirements of Column A and Column B of Table V.
    - (a) The second sample shall be of the size specified for the second sample in Table V for the size of lot undergoing testing, and shall be randomly selected from the units not previously tested.
    - (b) When the number of untested units is less than the number required by Table V, the second sample shall include all untested units and sufficient new samples random selected from the previously tested units to complete the number of samples required by Table IV for the second sample.
    - (c) Compute the COMBINED QUALITY INDEX from all of the test values for the combined first and second samples.
    - (d) ACCEPT THE LOT when the computed combined Quality Index equals or exceeds the Quality Index Requirement (k) of Column C, Table V for the size of lot undergoing quality assurance testing.
    - (e) REJECT THE LOT when the combined Quality Index equals or is less than the Quality Index Requirement of Column D, Table V or any individual value is less than the L value of Tables I and II.

#### 7.4 (Continued)

- (4) REJECT THE LOT when the film weight does not meet the requirement given in the QPL.
- g. Adhesive material of rejectable quality or unsatisfactory manufacturing characteristics may be subjected to chemical analysis in accordance with Section 5.2.e.

### 8.0 MATERIAL TEST METHODS

#### 8.1 General Bonding Procedure

- a. Adherend Preparation. Titanium 6Al-4V shall be 10 volt chromic acid anodized or equivalent\*.  
  
\*Surface must produce cohesive bonds and be thermally and environmentally stable.
- b. Priming
  - (1) Class I Type 1. Apply Class I Type 1 diluted with a 1:1 mixture of xylene and meta-creosol to 9 ± 1% solids by brush or spray to .0005 - .001" thickness. Dry in air circulating oven 120 minutes at 425 ± 10°F.
  - (2) Class II Type 1. Apply Class II Type 1 diluted with DMF to 26 ± 2% solids by brush or spray to .0005 - .001" thickness. Dry in air circulating oven 30 minutes at 150 ± 5°F followed by 60 minutes at 275 ± 5°F.
- c. Curing Test Assemblies. Place prepared assemblies in vacuum bag according to Figure 1 or equivalent. Cure and post cure in accordance with process spec.

#### 8.2 LAP Bond Shear

##### 8.2.1 Fabrication of Lap Bond Test Assemblies

- a. Fabricate test assembly by bonding two 6Al-4V titanium finger panels (see Figure 2) with Type 1 and Type 2 adhesives from the lots being tested.
- b. Prime each test panel with Type 1 adhesive within 16 hours of surface preparation.
- c. After drying Type 1 adhesive per 8.1.b., apply a strip of Type 2 film adhesive, approximately 0.75 inch wide and 6.5 inches long to the primed surface of one of each pair of test panels.
- d. Join the two test panels to make a test assembly having a lap joint with a 0.50 ± 0.03 inch overlap as shown in Figure 2.
- e. Embed a fine wire thermocouple (No. 30 maximum) in adhesive flash immediately adjacent to one overlap edge, in order to measure the curing temperature.

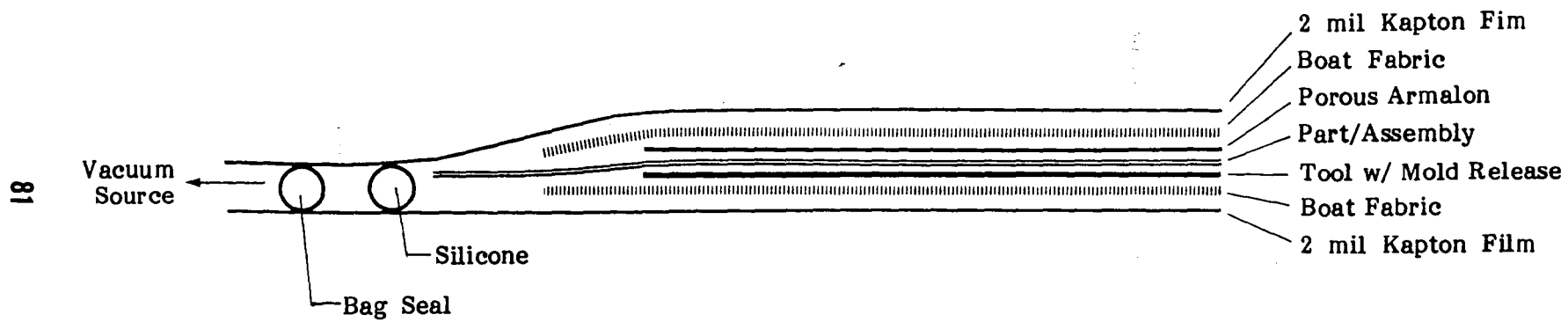


Figure 1 Bag for High Temperature Cures

TABLE IV

ASSEMBLIES AND SPECIMENS REQUIRED FOR  
ACCEPTANCE TESTS

	ASSEMBLIES	SPECIMENS
1. Shear at $75 \pm 5^{\circ}\text{F}$	1	5
2. Shear at $450 \pm 5^{\circ}\text{F}$	1	5
3. Flatwise Tensile at $75 \pm 5^{\circ}\text{F}$	1	5
4. Flatwise Tensile at $450 \pm 5^{\circ}\text{F}$	1	5
5. Percent Volatiles		2
6. Weight		2
7. Percent Solids Type 1 Only		2

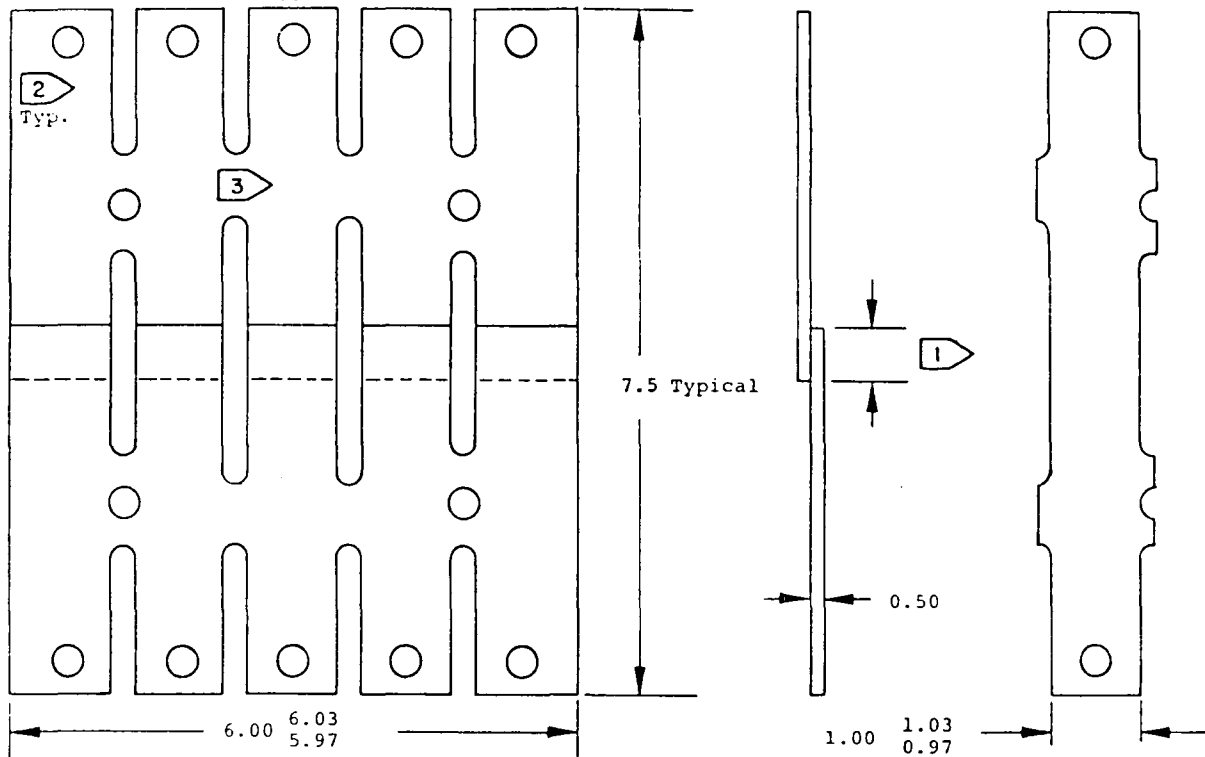
- f. Bag in accordance with Figure 1.
- g. Cure and post cure in accordance with process spec.

#### 8.2.2 Lap Bond Shear Test Specimens

- a. After cure cut test assemblies into individual test specimens.
  - (1) All cuts shall be accomplished so as to avoid overheating or mechanical damage to adhesive bond.
  - (2) Identify each specimen with the test assembly from which cut and with the lot of adhesive being tested.
  - (3) Trim excess adhesive from the side edges of each specimen.
- b. Any valid individual test value and the arithmetic mean of the test values shall equal or exceed the applicable minimum individual and average requirements in Table I or II. Any identifiable abnormality that cannot be attributed to adhesive performance invalidates a specimen.

#### 8.2.3 Lap Bond Shear Test Conditions

- a. These tests differ only in the conditioning given the test specimens before and during the time they are being tested. The following requirements are the same for each of the lap bond shear tests:
  - (1) The testing machine used to determine the lap bond shear strength shall have either vertical or horizontal, self-aligning grips which operate in such a manner, that with the test specimen properly positioned, an imaginary straight line passing through the center of the bonded area and parallel to the metal plates of the specimen would also pass through the center point of each grip mounting. Pin grips fitting the specimen end holes are recommended to prevent slippage.
  - (2) The testing machine shall have a loading range sufficient to insure a precision and accuracy of  $\pm 1$  percent within a loading range of 240 pounds to 2400 pounds. It shall meet requirements of ASTM Standards Specification E4-67.
  - (3) At the start of the test, each lap bond shear test specimen shall be positioned so that the inner edge of each grip shall be  $2.00 \pm 0.25$  inches from the nearest edge of the lap joint.



All dimensions in inches.

- 1 Except as otherwise specified the bond length shall be  $0.50 \pm 0.030$ .
- 2 Test assembly identification. Identify and number each specimen as necessary.
- 3 It is optional to notch for easy breakway without sawing.

STANDARD TEST ASSEMBLY AND SPECIMEN

Figure 2

- (4) Each lap bond shear test specimen shall be loaded in tension at the rate of 1200 to 1400 pounds per minute until the maximum loading is reached and the bond is broken. The maximum stress sustained by the specimen shall be expressed in pounds per square inch of bonded area. The area used for this calculation shall be the actual measured area of the overlap of the test specimen. The area shall be computed to the nearest 0.01 square inch and the tensile shear values obtained shall be rounded to the nearest 10 psi in accordance with the ASTM Standards E29-67.
- b. For Test No. 1, 4, 6 and 8 of Table I (normal temperature lap bond shear) and Test No. 1 of Table IV, the temperature of the test specimen shall be  $75 \pm 5^{\circ}\text{F}$ . The specimen shall be maintained within this temperature interval at least 1 hour before the test is made and at all times during the test. Test 4 shall be preceded by heat exposure of 500 hours at  $450 \pm 5^{\circ}\text{F}$ . Test 6 shall be preceded by heat exposure of 1000 hours at  $450 \pm 5^{\circ}\text{F}$ . Test 8 shall be preceded by heat exposure of 5000 hours at  $450 \pm 5^{\circ}\text{F}$ .
- c. For Test No. 2 of Table I (low temperature lap bond shear) the temperature of the metal at the bond line shall be  $-67 \pm 2$  degrees F for 10 minutes before the specimen is stressed and at all times after the stress is applied until the specimen is broken.
- d. For Test No. 3, 5, 7 and 9 of Table I (elevated temperature lap bond shear) and Test No. 2 of Table IV the temperature of the metal at the bond line shall be  $450 \pm 5^{\circ}\text{F}$  for 10 minutes before the specimen is stressed and at all times after the stress is applied until the specimen is broken. Test 5 shall be preceded by heat exposure of 500 hours at  $450 \pm 5^{\circ}\text{F}$ . Test 7 shall be preceded by heat exposure of 1000 hours at  $450 \pm 5^{\circ}\text{F}$ . Test 9 shall be preceded by heat exposure of 5000 hours at  $450 \pm 5^{\circ}\text{F}$ .
- e. For Test No. 14 of Table I (salt spray exposure), the salt solution, chamber, accessories, method of suspension, and general procedure shall be in accordance with Federal Test Method Standard No. 151, Method 811.1, "Salt Spray Test." Individually suspend each exposure specimen through one of the holes (see Figure 2).
- (1) The specimens shall remain in the salt spray at  $95 \pm 5^{\circ}\text{F}$  for 30 days  $\pm 2$  hours.
- (2) Within 4 hours after removal from the salt spray, test each of the specimens in lap shear at  $75 \pm 5^{\circ}\text{F}$ .
- (3) In addition to the individual specimen values and the average, report the following information:

- (a) Salt solution concentration.
  - (b) Type of salt and water used in preparation of the solution.
  - (c) All readings of temperature within the exposure zone of the chamber.
  - (d) Method of supporting specimen in the exposure chamber.
  - (e) Length of exposure
- f. For Test No. 15 of Table I (condensing humidity exposure), the water, humidity cabinet, method of suspension, and general procedure shall be in accordance with Federal Specification MMM-A-132.
- (1) The specimens shall remain in the condensing humidity atmosphere at  $120 \pm 5F$  for 30 days  $\pm 2$  hours.
  - (2) Within 4 hours after removal from the condensing humidity cabinet, test each specimen in lap shear at  $75 \pm 5F$ .
  - (3) In addition to the individual specimen values and grand average, report all temperature readings required by the test method.
- g. For Test No. 16 of Table I (jet fuel exposure), completely immerse each specimen in MIL-J-5161 Referee Fuel Grade 2 in such a manner that the test medium has equal access to all sides of the specimen. Faces of specimens immersed in the same container shall not contact each other.
- (1) The exposure section shall remain in the test medium at  $75 \pm 5F$  for 30 days  $\pm 2$  hours.
  - (2) Within 4 hours after removal from the test medium, test each specimen in lap shear at  $75 \pm 5F$ .
  - (3) Report all individual specimen values and the average.
- h. For Test No. 17 Table I (MIL-H-5606), the test conditions and procedures shall be the same as for Test 16 except the test medium shall be MIL-H-5606.
- i. For Test No. 18 Table I (MIL-H-7808), the test conditions and procedures shall be the same as for Test 16 except the test medium shall be MIL-H-7808.
- j. For Test No. 19 Table I (aircraft de-ice fluid), the test conditions and procedures shall be the same as for Test 16 except the test medium shall be aircraft de-ice fluid.

### 8.3 Lap Bond Fatigue

#### 8.3.1 Normal Temperature Lap Bond Fatigue

- a. Perform the normal-temperature Lap Bond Fatigue Test (No. 10) in accordance with the general provisions of Federal Test Method Standard No. 175, Method 1061 and the specific provisions indicated below:
  - (1) The test machine shall be capable of a cyclic axial load at the rate of  $1800 \pm 180$  cycles per minute.
  - (2) Loads shall be accurate within  $\pm 1$  percent.
  - (3) During each cycle the load shall range from a maximum to 10 percent of the maximum.
  - (4) The test specimens shall conform to the dimensional requirements of Figure 1.
- b. The temperature of the metal over the lap bond area shall be  $75 \pm 5F$  at all times during the test.
- c. At the start of the test, position each specimen with the overlap area equidistant between the grips of the test machine so that the edge of each grip will be  $2.00 \pm 0.13$  inches from the nearest edge of the bond.
  - (1) Test each specimen until  $10^6$  cycles at the particular maximum load have been completed or the specimen fails, whichever is sooner.
  - (2) Test a total of 10 test specimens, 5 from each of 2 test assemblies, using selected maximum loads such that failures occur with approximately regular spacing over the range of  $10^3$  to  $10^6$  cycles.
  - (3) Test at least one specimen at a maximum load of approximately 50% of the  $75 \pm 5F$  lap bond shear strength of Test No. 1.
- d. For each test, measure the actual bond area with a precision of  $\pm 1$  percent. Calculate the stress in psi corresponding to the maximum load. Plot the number of cycles until bond failure (log scale) and the corresponding maximum bond stress (arithmetic scale) on semi-log graph paper and draw a smooth curve through the plotted points. Extrapolate, if necessary, to the  $10^6$  cycles ordinate.
- e. Record and report all information called for by Federal Test Method Standard No. 175, Method 1061.

Report the fatigue strength as the stress corresponding to the point at which the curve through the plotted points crosses the  $10^6$  cycles ordinate.

### 8.3.2 Elevated Temperature Lap Bond Fatigue

Perform Fatigue Test No. 11 of Table I in accordance with Section 8.3.1 except for the conditioning prior to testing, the temperature during testing, and the maximum load which shall be 50% of the 450F strength of Test No. 3.

A suitable oven shall be provided to maintain the temperature at  $350 \pm 10\text{F}$  at all times during the testing.

### 8.4 Lap Bond Creep-Rupture-Deformation

#### 8.4.1 Normal Temperature Creep Test

- a. Perform the normal temperature creep-rupture-deformation test (No. 9 of Table I) on standard test specimens conforming to the dimensional requirements shown in Figure 1.
  - (1) Test the lap bond specimens in a "dead-weight" loading test apparatus capable of applying and maintaining a steady load accurate within 1 percent.
  - (2) The temperature of the specimen and the ambient temperature around it shall be  $75 \pm 5\text{F}$ .
  - (3) Apply a load of  $800 \pm 4$  pounds (1600 psi) to the specimen.
    - (a) Care must be taken to avoid eccentricity in the loading of the adhesive joint. Prior to testing, check the entire assembly of specimen and loading mechanism for alignment.
    - (b) Maintain the load for 192 hours or until rupture, whichever occurs first.
    - (c) Measurements of total deformation, including that due to initial loading, shall be made while the specimen is under stress.
    - (d) Measurements (to an accuracy of 0.0001 inch) shall be made at such time intervals that a smooth time-deformation curve may be plotted if deformations are large enough to permit.
  - (4) Measure the actual bond area with a precision of  $\pm 1$  percent and calculate actual stress.

8.4.1 (Continued)

- b. Record and report the following for each specimen:
  - (1) Lap bond area and stress.
  - (2) Deformation measurements and time for each.
  - (3) Time to failure, nature and percentage of each type of joint failure.
  - (4) Time-deformation curve (if deformations permit).

8.4.2 Elevated Temperature Creep Test

- a. The elevated temperature creep-rupture-deformation test (No. 11 of Table I) shall conform to the requirements of Section 8.4.1 with the following exceptions and/or additions:
  - (1) The temperature of the metal at the bond line shall be  $450 \pm 10$  F.
    - (a) The "temperature of the metal and the bond line" and the means for determining it shall be as prescribed in Section 8.1.5, Item c.
    - (b) A suitable oven, which does not influence the application of the load, shall be provided to maintain the required temperature.
  - (2) The applied load shall be  $400 \pm 2$  pounds (800 psi).
  - (3) Deformation need not be measured at  $450 \pm 10$  F. Measure deformation under the applied load before and after the heated period.
- b. Record and report the information required by Section 8.4.1, Item b.

## 8.5 Metal To Metal "T" Peel

### 8.5.1 Fabrication of T Peel Specimens

- a. Fabricate T peel specimens by bonding two 1"  $\pm$  .003 x 12" x 0.010" 6Al-4V titanium strips with Type 1 and Type 2 adhesives from lots being tested. See Sec. 8.1, General Bonding Procedure.
- b. Prime each test strip with Type 1 adhesive within 16 hours of surface preparation.
- c. After drying Type 1 adhesive per 8.1.b apply a strip of Type 2 film adhesive 1" wide by 10 inches long. See Figure 4.
- d. Bag in accordance with Figure 1.
- e. Cure and post cure per process spec.
- f. Identify each specimen with specimen no. and lot of adhesive being tested.
- g. Trim excess adhesive from edges of specimens.

### 8.5.2 T-Peel Test Conditions

- a. These test differ only in the conditioning given test specimens before and during the time they are being tested. The following requirements are the same for each T-peel specimen tests:
  - (1) The testing machine shall be capable of applying a tensile load having the following prescribed conditions.

- 8.5.2.1
  - a. The machine and loading range shall be so selected that the maximum load on the specimen falls between 15 and 85 percent of the upper limit of the loading range.
  - b. The rate of movement between heads shall remain essentially constant under fluctuating loads.

NOTE: It is difficult to meet this requirement when loads are measured with a spring-type or pendulum-type weighing device.
  - c. The machine shall be equipped with suitable grips capable of clamping the specimens firmly and without slippage throughout the tests.
  - d. The machine shall be autographic, giving a chart that can be read in terms of inches of separation as one coordinate and applied load as the other coordinate.
  - e. The applied tension as measured and recorded shall be accurate within - 1 percent.

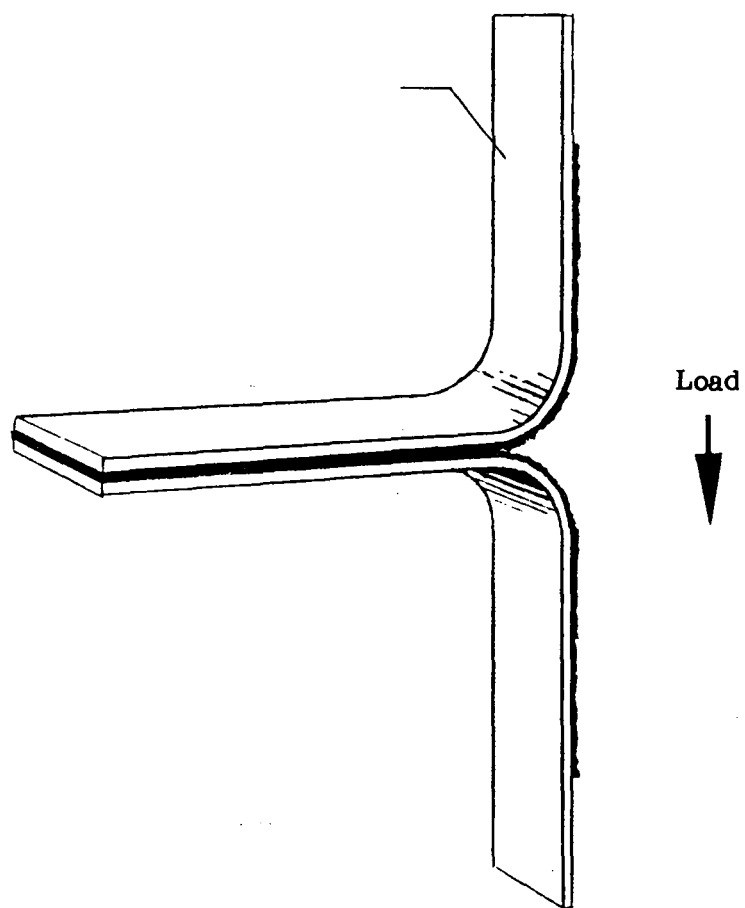
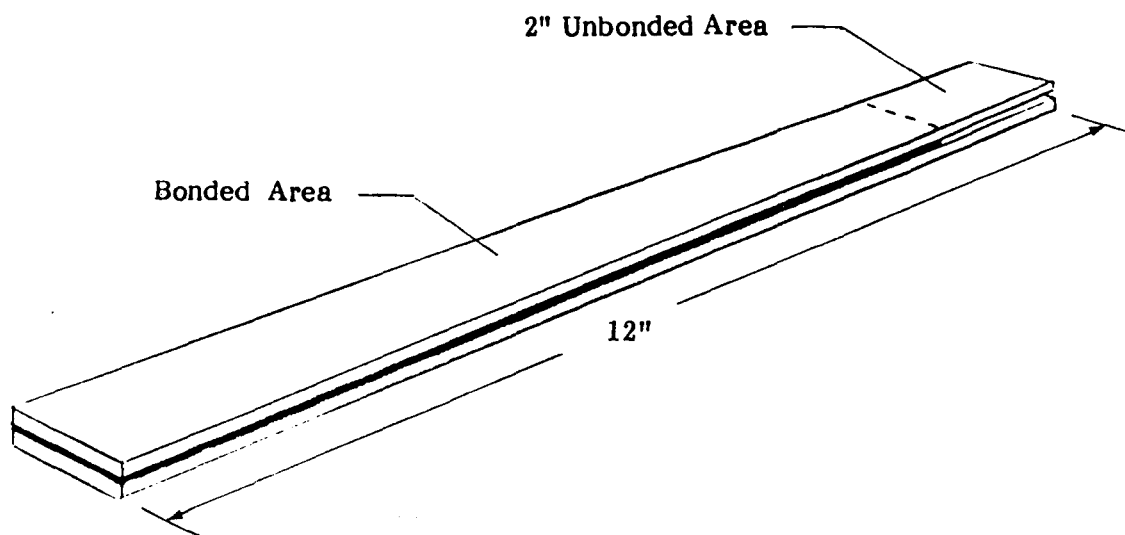


Figure 4 T-Peel

- 8.5.2.2 Test Procedure. Clamp the bent, unbonded ends of the test specimen in test grips of tension testing machine. Apply the load at a constant head speed of 10 in/min. During the peel test make an autographic recording of load versus head movement or load versus distance peeled. Determine the peel resistance over at least 5 inches length of the bond line after the initial peak.
- 8.5.2.3 Calculation. Determine from the autographic curve the average peeling load in pounds per inch of specimen width required to separate the adherends. Report value as pounds per 1 inch width.
- 8.5.3 For Test No. 20 and 22 of Table 1 (Normal Temperature T-Peel) the temperature of the test specimen shall be  $75 \pm 5^{\circ}\text{F}$ . The specimen shall be maintained within this temperature range at least one hour before the test is made and at all times during the test. Test 22 shall be preceded by heat exposure of 1000 hours at  $450 \pm 10^{\circ}\text{F}$ .
- 8.5.4 For Test No. 21 and 23 of Table I (Elevated Temperature T-Peel Test) the temperature of the metal at the bond line shall be  $450 \pm 10^{\circ}\text{F}$  for 10 minutes before the specimen is stressed and at all times after the stress is applied until the test is complete. Test No. 23 shall be preceded by heat exposure of 1000 hours at  $450 \pm 10^{\circ}\text{F}$ .

## 8.6 Environmental Durability Test

### 8.6.1 Crack Extension Specimen Fabrication

- a. Fabricate crack extension specimens by bonding two  $1.0 \pm .003$ " x 6" + 0.050" 6AL-4V titanium parts with Type 1 and Type 2 adhesive from lots being tested.
- b. Prime each test part with Type 1 adhesive within 16 hours of surface preparation.
- c. After drying Type 1 adhesive per 8.1.b apply a strip of Type 2 film adhesive 1" wide by 5.50" long. See Figure 5.
- d. Bag in accordance with Figure 1.
- e. Cure and post cure per process spec.
- f. Identify each specimen with specimen no. and lot of adhesive being tested.
- g. Trim excess adhesive from edges of specimens and sand, grind or mill one edge of specimen so crack tip can be easily seen.

#### 8.6.2 Crack Extension Test Conditions

- a. Precrack the end end of the specimen in which the adhesive was omitted by inserting a .125" wedge as shown in Figure 5.
- b. Locate and mark the tip of the initial crack.
- c. Tests 1, 2 and 3 of Table III differ only in the conditioning given the specimens after the initial crack tip is marked. Test 1 specimens shall be aged at  $75 \pm 5^{\circ}\text{F}$  for 1000 hours. Test 2 specimens shall be aged at  $120^{\circ}\text{F}$  in 95-100% relative humidity for 1000 hours.
- d. At the end of the exposure time mark the new crack tip, measure the distance from the initial crack tip to the nearest .05" and record that measurement.

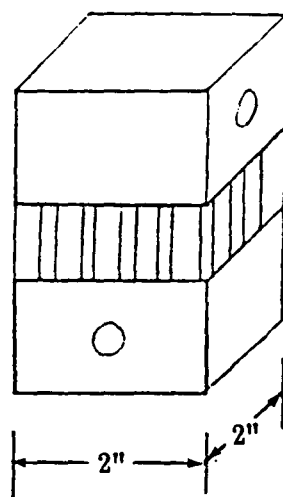
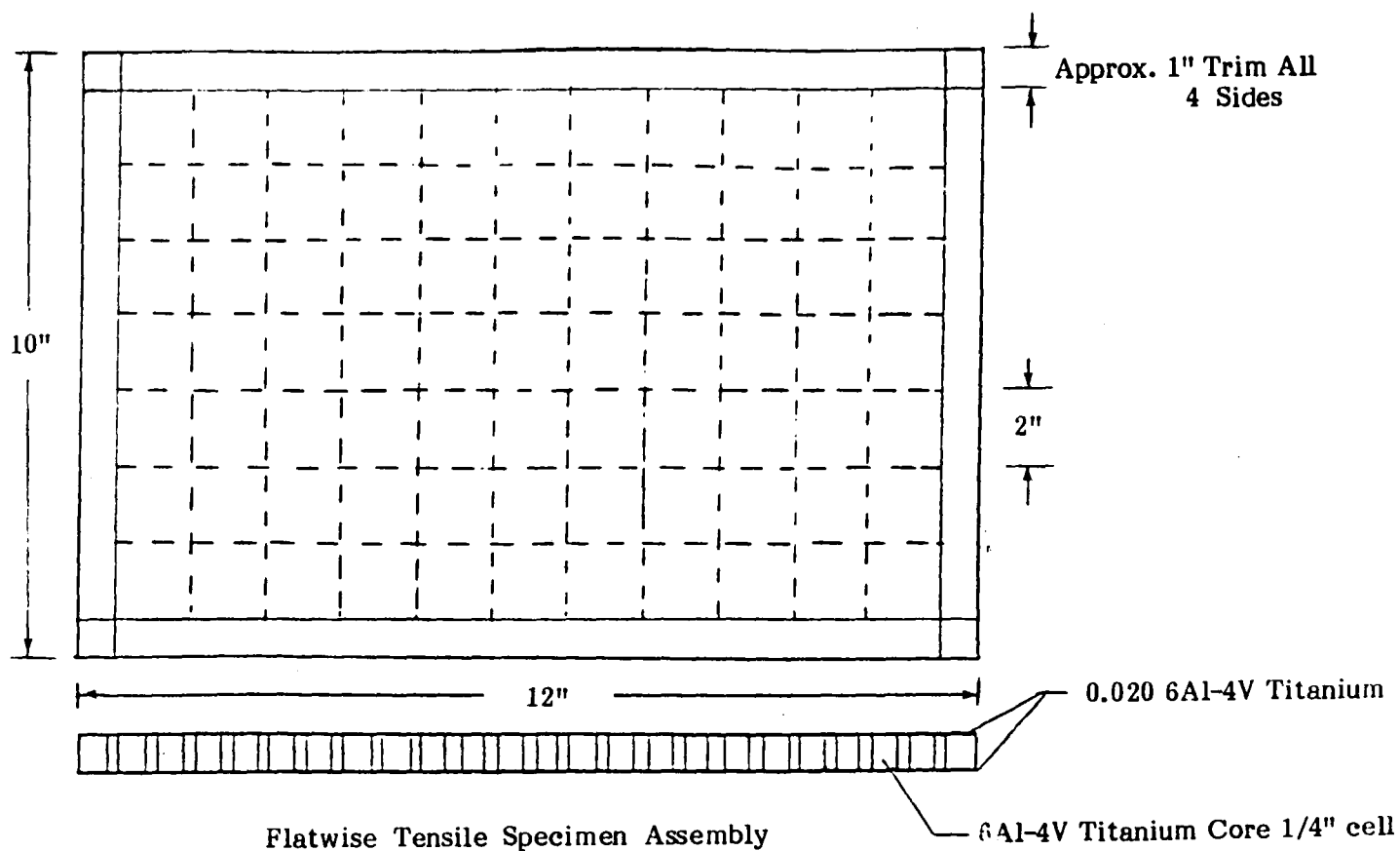
#### 8.6.3 Lap Shear Sustained Stress Loading

- a. Fabricate lap shear specimens per Sec. 8:2.
- b. Put a sustained load of 1200 psi on each specimen and expose to  $120 \pm 5^{\circ}\text{F}$  and 95-100% relative humidity for 2000 hours.

### 8.7 Honeycomb Specimens

#### 8.7.1 Flatwise Tensile Test

- a. Specimen Fabrication
  - (1) Fabricate specimens by bonding two 6AL-4V titanium skins 0.020" thick to 6Al-4V titanium honeycomb core (1/4" cell) (see Figure 5) with Type 1 and Type 2 grade - adhesive.
  - (2) Clean titanium core and skins and bond according to Sec. 8.1.
  - (3) Cut cured assembly into 2" x 2" specimens. All cuts shall be accomplished so as to avoid overheating or mechanical damage to adhesive bonds.
  - (4) Identify each specimen with the test assembly from which cut and with the lot of adhesive being tested.
- b. Test Conditions
  - (1) Environmental exposure shall be performed on 2" x 2" test specimens before bonding them to attachment blocks.
  - (2) For test No. 4 and 5 of Table II shall be exposed  $350 \pm 5^{\circ}\text{F}$  for 1000 hrs. before testing.
  - (3) Bond load block to specimen (Figure 5) by vacuum blasting surfaces and bonding with HR 424 structural adhesive.



Flatwise Tensile Specimen With Load Blocks

Figure 5

8.7.1 (Continued)

- (4) Normal temperature test (No. 1 and 4 of Table II) shall be performed at  $75 \pm 5^{\circ}\text{F}$  with load blocks within. This temperature range for at least 30 minutes prior to test.
- (5) Low temperature test (No. 2 of Table II) shall be performed at  $-65 \pm 5^{\circ}\text{F}$  with load blocks maintained at this temperature range for at least 30 minutes prior to test.
- (6) Elevated temperature test (No. 3 and 5 of Table II) shall be performed at  $450 \pm 10^{\circ}\text{F}$  with load blocks maintained at this temperature range for at least 30 minutes prior to test.

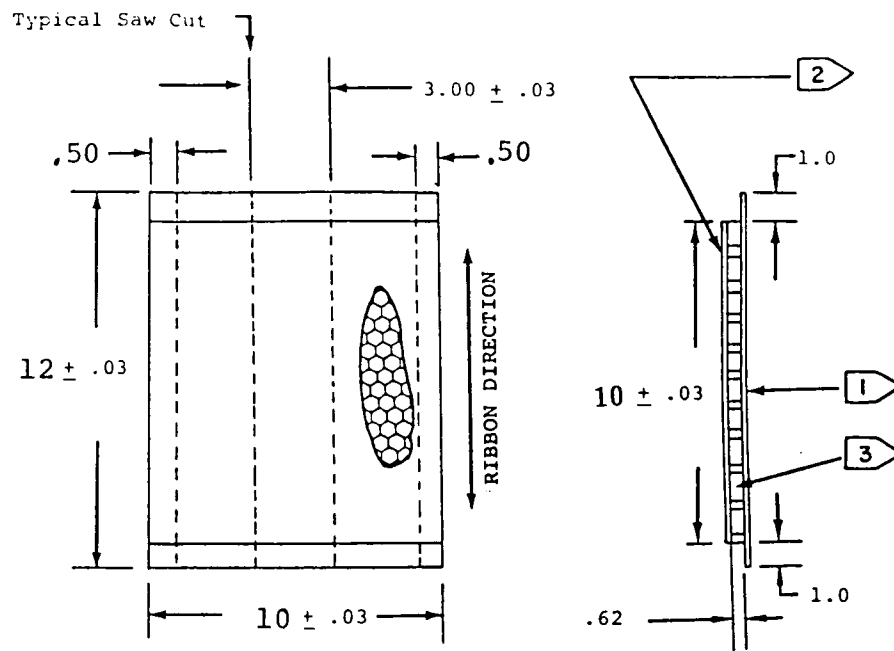
8.7.2 Honeycomb Peel Test

a. Honeycomb Peel Specimen Fabrication

- (1) Fabricate specimens by bonding two 6Al-4V titanium skins (one  $12 \times 10 \times .010$  and one  $10 \times 10 \times .010$ ) to a  $10" \times 10"$  piece of 6Al-4V titanium honeycomb core ( $1/4"$  cell) with Type 1 and Type 2 grade - adhesive.
- (2) Clean skins and core and bond according to Sec. 8.1.
- (3) Cut assemblies into specimens per Figure 6. All cuts shall be accomplished so as to avoid overheating on mechanical damage to the adhesive loads.
- (4) Identify each specimen with test assembly from which cut and lot of adhesive being testing.

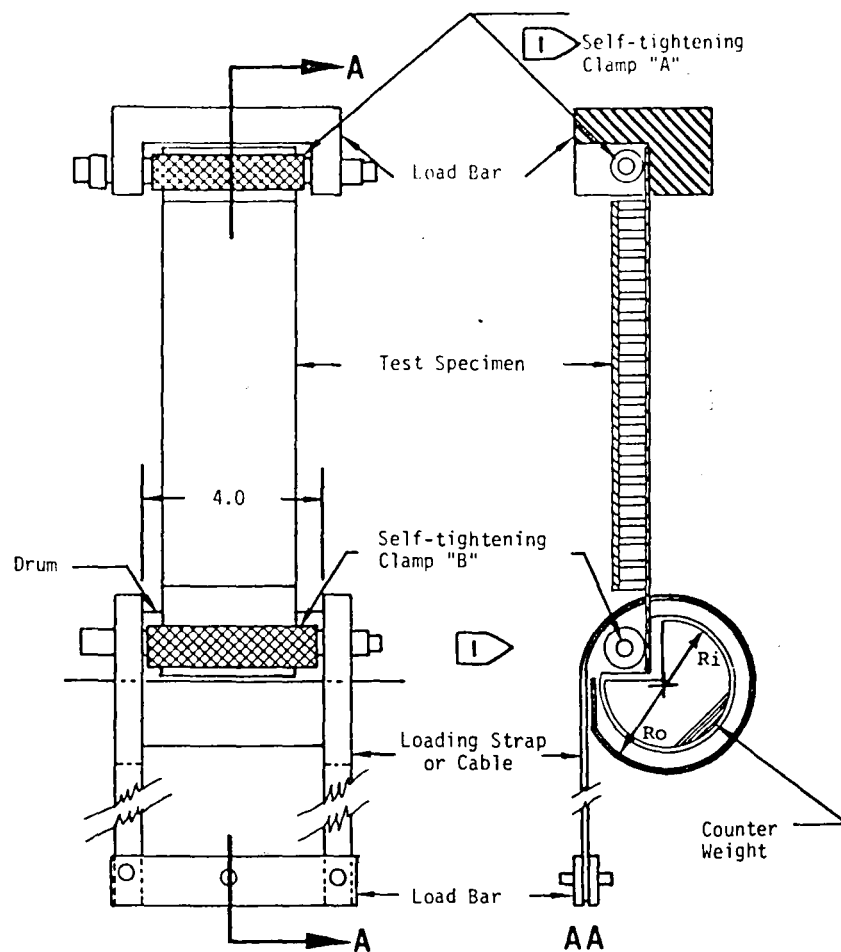
b. Honeycomb Peel Test Conditions

- (1) Normal temperature test (Test No. 6, Table II) shall be performed at  $75 \pm 5^{\circ}\text{F}$  with specimen held within this temperature range for at least 30 minutes prior to and during test.
- (2) Elevated temperature test (Test No. 7 Table II) shall be performed at  $450 \pm 5^{\circ}\text{F}$  with specimen held within this range at least 30 minutes prior to and during test.
- (3) Place specimen in climbing drum peel apparatus according to Figure 7.
- (4) Apply a tensile load at a crosshead speed of  $3.00 \pm 0.30$  inches per minute and make an autographic recording of the load.
- (5) Report values as peel strength in pound-inches per 3 inches of specimen width.



- 1 Peeling Face Panel - 10.0 x 12.0 x 0.010 inches
- 2 Backing Panel - 10.0 x 10.0 x 0.010 inches
- 3 Core - 10.0 x 10.0

Figure 6 Honeycomb Peel Assembly and Specimen.



All dimensions in inches

$$R_1 = 2.000 \pm 0.005$$

$$R_0 = 2.500 \pm 0.005$$

SCHEMATIC DIAGRAM

HONEYCOMB CLIMBING DRUM PEEL TEST APPARATUS

FIGURE 7

I Other clamping devices may be used.

## 8.8 Weight (Type 2 Adhesive Only)

- a. Adhesive weight measurements are made on a  $36 \pm 0.36$  square inch specimen from which the separator sheet has been removed.
  - (1) At least two specimens shall be cut from each qualification sample.
  - (2) Specimens shall be taken at random except that no specimen shall include areas closer than 1 inch from the edge of the roll.
- b. After the specimen has been weighed to the nearest 0.1 gram, calculate the weight of the adhesive as follows:
  - (1)  $W = 0.00882 S$   
Where:  
 $W$  = Weight (pounds per square foot)  
 $S$  = Sample weight in grams
  - (2) The calculated weight shall be expressed to the nearest 0.001 pound per square foot in accordance with ASTM Standards E29-
- c. Report all test data and the average for each sample.

## 8.9 Percent Solids (Type 1 Adhesive Only)

The percent solids indicated on the Type 1 adhesive containers is  $81 \pm 3$  percent. This is the correct percentage for formulation. When this adhesive is heated above 300F the condensation reaction begins and volatile products are released. Therefore, for test purposes the percent solids shall be  $76 \pm 3$  percent.

- a. Tare weight two suitable containers for each batch of adhesive in the qualification samples (or lot in the case of Purchaser Inspection).
- b. Weight  $15 \pm 2$  grams of well mixed adhesive into each container.
- c. All weighing shall be to the nearest 0.1 gram.
- d. Heat in a controlled oven at  $450 \pm 10$  F for 1 hour, followed by 1 hour at  $500 \text{ F} \pm 10\text{F}$ .
- e. Cool in a desiccator and weigh.
- f. Report the percent solids as a weight percentage of the original test sample weight.
- g. Report all test data and the average for each qualification (or lot) sample.

## 9.0 MATERIAL IDENTIFICATION

- a. Each metal container and roll of adhesive shall be legibly identified and labeled with the items of information listed below. The rolls of adhesive shall have the identification label, or marking, on the inside of the core. Metal containers shall have the identification securely affixed to the container.
  - (1) Specification Number, Type and Grade of the adhesive.
  - (2) Supplier's Name and Address.
  - (3) Supplier's Batch Number.
  - (4) Date of Manufacture.
  - (5) Purchase Order Number.
  - (6) Unit Number of Roll.
- b. Both ends of the exterior (shipping) package of all adhesives covered by this specification shall be legibly marked on the outside with the following information.
  - (1) Specification Number and Type of the Adhesive.
  - (2) Purchase Order Number.
  - (3) Supplier's Name and Address.
  - (4) Supplier's Batch Number.
  - (5) Date of Manufacture.
  - (6) Quantity in this Package.
  - (7) Date of Shipment.

## 10.0 PACKAGING AND MARKING

- a. Type 1 adhesive shall be packaged in clean, air-tight one quart metal containers.
- b. Each roll of Type 2 Film Adhesive shall be sealed air-tight in a flexible, vapor barrier bag made of a material qualified to MIL-B-131 for Class 1.
- c. The core of each roll of Type 2 Film Adhesive shall contain sufficient desiccant to insure there will be no degradation of the adhesive from water vapor entrapped within the sealed wrapper during the warranty period.
- d. The amount of material in each roll of Type 2 Film Adhesive may be adjusted to be compatible with the production cycle of manufacturer, except that the normal roll length shall be at least 20 yards with a minimum width of 36 inches unless otherwise specified on the purchase order.

## 10.0 (Continued)

- e. The exterior packaging for all types shall be of such a nature as to prevent physical damage or contamination by foreign substances.
  - (1) Each package shall be suitably insulated and refrigerated, when necessary, to insure maintenance of the shipping temperature requirements.
  - (2) The exterior packaging for Type 2 Film Adhesive shall be free of fasteners which could damage or puncture the vapor barrier wrapper.
  - (3) Support the ends of the core of each roll of Type 2 Film Adhesive, within the exterior packaging, in such a manner as to prevent damage to the vapor barrier wrapper and contact with the sides of the exterior package.

## 10.1 Shipping Temperature

The shipping temperatures for Type 1 and Type 2 adhesives shall be as specified in Section 5.1.3.

**End of Document**